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NANO COMPOSITE OF CLAY MODIFIED KETONIC RESIN AS FIRE RETARDANT POLYOL FOR POLYURETHANE

M.Sc. THESIS

Derya ÖNEN
(515131006)

Department of Polymer Science and Technology

Polymer Science and Technology Programme

Thesis Advisor: Prof. Dr. Nilgün KIZILCAN

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YÜKSEK LİSANS TEZİ

Derya ÖNEN
(515131006)

Polimer Bilim ve Teknolojisi Anabilim Dalı

Polimer Bilim ve Teknolojisi Programı

Tez Danışmanı: Prof. Dr. Nilgün KIZILCAN

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Derya Önen, a **M.Sc.** student of ITU **Polymer Science and Technology** student ID **515131006**, successfully defended the **thesis** entitled "**NANO COMPOSITE OF CLAY MODIFIED KETONIC RESIN AS FIRE RETARDANT POLYOL FOR POLYURETHANE**", which she prepared after fulfilling the requirements specified in the associated legislations, before the jury whose signatures are below.

Thesis Advisor :	**Prof. Dr. Nilgün KIZILCAN** İstanbul Technical University	.....
Jury Members :	**Prof. Dr. Ayfer SARAÇ** Yıldız Technical University	.....
	Prof. Dr. Ahmet AKAR Istanbul Technical University	.....

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To my parents and fiancé,

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Derya ÖNEN
Chemical Engineer

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ABBREVIATIONS

CFR	**:** Cyclohexanone-Formaldehyde Resin
Sep1-CFR	**:** Cyclohexanone-Formaldehyde Resin Modified With 1% Sepiolite
Sep3-CFR	**:** Cyclohexanone-Formaldehyde Resin Modified With 3% Sepiolite
Sep5-CFR	**:** Cyclohexanone-Formaldehyde Resin Modified With 5% Sepiolite
MM1-CFR	**:** Cyclohexanone-Formaldehyde Resin Modified With 1% Montmorillonite
MM5-CFR	**:** Cyclohexanone-Formaldehyde Resin Modified With 5% Montmorillonite
AA5-CFR	**:** Cyclohexanone-Formaldehyde Resin Modified With 5% Alendronic Acid
AA10-CFR	**:** Cyclohexanone-Formaldehyde Resin Modified With 10% Alendronic Acid
AA20-CFR	**:** Cyclohexanone-Formaldehyde Resin Modified With 20% Alendronic Acid
Sep7.5-AA10-CFR	**:** Cyclohexanone-Formaldehyde Resin Modified With 7.5% Sepiolite and 10% Alendronic Acid
Sep20-AA10-CFR	**:** Cyclohexanone-Formaldehyde Resin Modified With 20% Sepiolite and 10% Alendronic Acid
MM5-AA5-CFR	**:** Cyclohexanone-Formaldehyde Resin Modified With 5% Montmorillonite and 5% Alendronic Acid
MM10-AA10-CFR	**:** Cyclohexanone-Formaldehyde Resin Modified With 10% Montmorillonite and 10% Alendronic Acid
PU	**:** Polyurethane

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NANO COMPOSITE OF CLAY MODIFIED KETONIC RESIN AS FIRE RETARDANT POLYOL FOR POLYURETHANE

SUMMARY

Polyurethanes (PU) are used in many application areas in daily life. They are very important polymers since they are highly inclined to modification. Polyurethanes have isocyanate linkages and they are synthesized by the reaction of isocyanate and polyol. They can be produced in thermoplastic or thermoset form, however mostly they are thermosets. One of the most important characteristic properties of polyurethane is that they can be produced as foam. Polyurethane foams can be analyzed in two groups as flexible and rigid polyurethane foams. A blowing agent is required for cell formation and blowing action. As foams are lightweight, resistant to moisture and have low thermal conductivity, these foams are generally used in insulation industry. They are very successful to maintain uniform temperature; however, high flammability of foam polyurethane is a risk in case of a fire. The aim of this study is to supply fire resistance to rigid foam polyurethane. Firstly, cyclohexanone-formaldehyde resin (CFR), which is a ketonic resin, is synthesized in the laboratory. NaOH is the catalyst of polymerization. After synthesizing unmodified CFR as reference material, clay and phosphonate modified CFRs are synthesized. Sepiolite and montmorillonite are the clays that are used for modification of CFR. These clays are utilized in powder form. Hence, resulting resins can be called as nanocomposite or nanoclay modified CFR. Sepiolite is a hydrated magnesium silicate clay. The structure of sepiolite contains ribbons of a 2:1 phyllosilicate structure. Montmorillonite is a layered silicate, which has very thin layers that are bound together by counter-ions They have high water absorption capacity, high aspect ratio and high surface area. As phosphonate, alendronic acid is used in CFR synthesis. The reactants of CFR, which are cyclohexanone and formaldehyde, are mixed with modifier i.e clay or alendronic acid in the beginning of the polymerization reaction. Due to the procedure, the reaction is in-situ polymerization. Reactants and modifier are uniformly mixed with reactants and catalyst and heat is applied as the reaction proceeds. After all, thirteen different resins are synthesized. CFR with sepiolite as 1%, 3% and %5, CFR with montmorillonite as 1% and %5, CFR with alendronic acid as 5%, 10% and 20%. By synthesis of these resins, effects of the percentage of modifiers on resin and polyurethane are investigated. After that, CFR is modified with mixture of clays and alendronic acid. These resins include CFR with 5% montmorillonite and 5% alendronic acid, CFR with 10% montmorillonite and 10% alendronic acid, CFR with 7.5% sepiolite and 10% alendronic acid and finally CFR with 20% sepiolite and 10% alendronic acid. All resins are washed with water and dried in a vacuum oven after polymerization is complete. They are crashed and shaped in powder form. These resins are dissolved in dichloromethane, which is a powerful solvent, and mixed with polyol. As polyol and resin mixture is homogeneous, isocyanate is added to the mixture and stirred for a very short time. Rigid polyurethane foams, modified by

flame retardant CFRs, are polymerized and puffed up. In order to characterize the resins, FTIR-ATR, NMR, XRD and TGA methods are used. By FTIR characterization, it is concluded that nanocomposite modified CFRs and alendronic acid modified CFRs are synthesized successfully. XRD results indicated that sepiolite modified CFRs have exfoliated structures, while montmorillonite modified CFRs have intercalated structures. It is observed that alendronic acid acts as a compatibilizer between clay and resin matrix. In TGA results, it is concluded that the heat resistance of CFR is increased by addition of both alendronic acid and nanocomposite of clay. As the alendronic acid and clay concentration increase, heat resistance of resin increases as well. LOI analysis of PU foams indicated that AA10-CFR, Sep5-CFR and MM5-AA5-CFR have higher LOI than CFR. Therefore, PU with AA10-CFR,, Sep5-CFR and PU with MM5-AA5-CFR are more resistant to fire. In conclusion, MM5-AA5-CFR is the best nanocomposite additive to fire resistant PU foam.

NANO KOMPOZİT KİL İLE MODİFİYE EDİLMİŞ KETONİK REÇİNENİN YANGIN GECİKTİRİCİ OLARAK POLİOLDE KULLANILMASIYLA POLİÜRETAN SENTEZİ

ÖZET

Bu tezin amacı kil ve fosfonat ile modifiye edilmiş siklohekzanon-formaldehit reçinesi sentezleyerek reçineyi modifiye etmek ve modifiye reçineleri poliüretan sert köpük sentezinde kullanarak poliüretana yanmazlık özelliği kazandırmaktır.

Poliüretan, izosiyanat ve poliolün birbirleriyle reaksiyona girmesi sonucu sentezlenir. Otomotiv sektöründe, yapıştırıcılarda, mobilyalarda, beyaz eşyalarda ve daha birçok alanda kullanılırlar. En önemli özelliklerinden biri köpük olarak üretilebilmesidir. Sert, yarı-sert ve yumuşak poliüretan köpük olarak sınıflandırılabilirler.

Sert poliüretan köpük çok kullanışlı bir polimer olmasına rağmen çok hızlı yanma özelliğine sahiptir. Özellikle yalıtım sektöründe kullanılan poliüretan sert köpük, binaların cephelerine uygulanarak ısı bina içinde hapsedilir. Kullanımı avantajlıdır, çünkü düşük yoğunluğu vardır, uzun ömürlüdür ve birçok kapalı hücreden oluşur. Kapalı hücreler şişirici ajanlarla doludur ve bu gazların ısı iletkenlikleri çok düşüktür. Bu sebeple sert köpük poliüretan ısı yalıtımında verimlidir; ancak olası bir yangın durumunda ise yüksek yanabilirliği olan bu malzeme çok büyük bir risk teşkil etmektedir. Bu sebeple, poliüretana yanmazlık özelliği kazandırmak için üzerine birçok bilimsel çalışma yapılmıştır.

Bu tezde, poliüretan sert köpüğe yanmazlık özelliği sağlamak için öncelikle siklohekzanon-formaldehit reçinesi sentezlenmiştir. Siklohekzanon-formaldehit reçinesi ketonik ve termoplastik bir reçinedir. Kondenzasyon reaksiyonu sonucu oluşur ve siklik yapıdadır. Polar çözücülerde iyi çözünür. Kaplama sektöründe kullanılır.

Bu çalışmanın ilk adımı siklohekzanon-formaldehit reçinesinin sentezidir. Siklohekzanon ve formaldehit karıştırılarak üç boyunlu bir balona konulmuştur. Siklohekzanonun çözünürlüğünün artması için ortama bir miktar siklohekzan eklenmiştir. Reaksiyonun katalizörü sodyum hidroksittir, bu sebeple reaksiyonu başlatmadan önce %20'lik sodyum hidroksit çözeltisi hazırlanmıştır. Üç boyunlu balon altında ısıtıcı olan bir yağ banyosuna oturtturulmuş, mekanik karıştırıcı balona bağlanmış ve balon standa sabitlenmiştir. Boyunlardan birine geri soğutucu bağlanmıştır. Diğer boyun ise cam kapakla kapatılmış ve reaksiyon için sistem hazır hale getirilmiştir. Sistem ısınmaya başlayınca, karışıma hazırlanan %20'lik sodyum hidroksit çözeltisi damla damla eklenmiş ve sistemin pH'ı 12'ye sabitlenmiştir. Reaksiyon başladığından dolayı pH zamanla düşme eğilimindedir, bu sebeple kısa aralıklarla pH kontrol edilmiştir. Reaksiyon 60°C'ye gelince, riflaks başlar. Riflaks başladığı zaman cam kapak çıkartılmış ve buradan sisteme formaldehit damla damla olacak şekilde sisteme eklenmiştir. Formaldehit eklenmesi bitince pH kontrolü yapılmalıdır, çünkü bu aşamada reçineleşme gözlemlenmiştir. Karışımın rengi şeffaftan sarıya dönmeye başlar. Düşen pH tekrar %20'lik sodyum hidroksit ile 12ye, sıcaklık ise 80°C'ye sabitlenir. Reçinenin reaksiyon süresi beş saattir. Bu süre sonunda reaksiyon ısıtıcı ve karıştırıcıyı kapatarak sonlandırılmış ve reçine su ile yıkanmıştır. Öncelikle etüvde 80°C'de beş saat kurutulan reçine, vakum etüvünde tekrar kurutulmuştur. Kuruyan reçine toz haline getirilmiştir.

Siklohekzanon-formaldehit reçinesi eş zamanlı olarak sepiyolit ve montmorillanit ile modifiye edilmek üzere birçok kez sentezlenmiştir. Sepiyolit filosilikat yapılı bir kildir. Yüksek emme kapasitesi ve düşük termal kondaktivitesi vardır. Özellikle

Türkiye'nin Eskişehir bölgesinde bulunur. İğne şeklinde yapısı vardır. Montmorillanit ise bentonitten elde edilen bir kildir. Katmanlı bir yapısı vardır. Her biriminde iki tetrahedral ve bir oktahedral katmanı vardır ve yüksek su emme kabiliyeti bulunmaktadır. Killer, reaksiyon başlatılmadan önce siklohekzanon, siklohekzan ve formaldehit karışımıyla karıştırılmış ve polimerizasyon başlatılmıştır. Modifiye reçine deneylerinin geri kalanı, tamamen siklohekzanon-formaldehit reçinesinin senteziyle aynıdır. Sepiyolit modifiyeli reçine %1, %3 ve %5'lik olarak sentezlenmiştir. Montmorillanit modifiyeli reçine ise %1 ve %5'lik olmak üzere sentezlenmiştir. Sepiyolitli reçineler sarı ve açık kahverengi renk almışken, montmorillanitli olanlar beyaza daha yakın bir renk almışlardır.

Alendronik asit ilaç sektöründe kullanılan bir kimyasaldır. Osteoporoz, halk arasında bilinen adıyla kemik erimesi tedavisinde kullanılır. Halojen içeren yangın geciktiricilere göre daha tercih edilesi bir alternatiftir, çünkü toksisitesi daha azdır. Siklohekzanon-formaldehit reçinesi modifikasyonu için %5, %10 ve %20'lik olmak üzere üç ayrı reçine sentezlenmiştir. Reçineler modifiye edilmemiş siklohekzanon-formaldehit reçinesine göre daha sarı renk almışlardır ve alendronik asit yüzdesi arttıkça sarı renk daha baskın olmuştur.

Siklohekzanon-Formaldehit reçinesi kil ve fosfonat karışımıyla da modifiye edilmiştir. Bunun için reçinenin reaktantları ile kil ve alendronik asit karıştırılmış ve reaksiyon başlatılmıştır. Diğer reçine sentezleriyle aynı deney prosedürü izlenmiştir. Sentezlenen reçineler %5 montmorillanit ve %5 alendronik asitli, %10 montmorillanit ve %10 alendronik asitli, %7.5 sepiyolit ve % 10 alendronik asitli ve son olarak %20 sepiyolit ve %10 alendronik asitlidir. Bu reçinelerin modifikatörleri fazla olduğu için viskoziteleri daha yüksek ve renkleri daha koyudur.

Alendronik asitli reçineler, ince film kromatografisi (TLC) ile nitelik olarak karakterize edilmiştir. Karakterizasyon için %60 hekzan, %40 etil asetat ve %1 metanol solvent olarak kullanılmıştır. TLC sonucuna göre alendronik asit modifiyeli CFR'nin CFR'den tamamen farklı olduğu ve ürünün sadece modifiye edilmiş reçine olduğu gözlemlendi.

Reçinelerin karakterizasyonu için FTIR kullanılmıştır. FTIR sayesinde nanokompozitlerin bağları incelenmiştir.

Reçinelerin çeşitli solventlerde çözünürlüklerine bakılmıştır. Bu solventler dikolorometan, dimetil-formamid, tetrahidrofuran, dimetil-sülfoksit, kloroform, metanol ve asetondur.

Çözünürlük testinde reçinelerin çoğunun diklorometanda çözündüğü gözlemlenmiştir. Reçinelerin NMR analizinin yapılması için reçineler dötero diklorometanda çözünmüştür.

Reçinelerin erime noktaları, Erime Noktası Tayin Cihazıyla ölçülmüştür.

Killerin reçinedeki dağılımını incelemek için XRD karakterizasyon yöntemi kullanılmıştır. XRD ile reçine kristalleri arasındaki mesafeler hesaplanmıştır. Böylelikle killerin reçinede homojen dağılım elde edip etmediği görülmüştür. Sonuç olarak, montmorillantın CFR içinde interkalasyona uğrarken, sepiyolitin ise eksfoliasyona uğradıkları görülmüştür. Ayrıca alendronik asit kil ve reçine karışımına eklendiğinde, reçinenin daha fazla kil ile doyurulabiliceği gözlemlenmiştir. Bu sebeple alendronik asit kil ve reçine arasında kompabilizatör görevi üstlenmiştir.

Reçine karakterizasyonunda son adım TGA'dır. Reçinelerin TGA bozunma eğrileri incelenmiş, yarılanma sıcaklıkları ve 700°C'de kalan madde miktarı araştırılmıştır. Sonuç olarak, alendronik asitin ve killerin reçinenin ısıya dayanıklılığını arttırdığı

gözlemlenmiştir. Kil ve alendronik asit yüzdesi arttıkça reçine yanmaya daha dayanıklı olmuştur.

Poliüretan sert köpük sentezi için önce reçine diklorometanda çözülmüştür. Çözünen reçine, poliol ile mekanik karıştırıcıda iki dakika karıştırılarak homojen karışım sağlanmıştır. Karışımdaki reçine, karışımdaki poliolün kütlece %60'ı kadardır. Poliol ve izosiyanat kütlesel olarak 1:1.2 oranında olacak şekilde on beş saniye mekanik karıştırıcı ile karıştırılmıştır. Bir süre sonra kap ısınmaya başlamış, karışım kabarmaya başlamıştır ve gaz çıkışı gözlemlenmiştir. Bu gaz poliüretanın şişmesini ve gözenekli yapıyı sağlamıştır. Şişme durduğu zaman poliüretan sertleşmiş ve son halini almıştır.

Poliüretan sert köpüklerde, sentezlenen reçinelerden altı tanesi kullanılmıştır. Bunlar siklohekzanon-formaldehit reçinesi ve %10 alendronik asitli, %20 alendronik asitli, %7.5 sepiyolit ve %10 alendronik asitli, %5 montmorillanit ve %5 alendronik asitli ve %5 sepiyolitli modifiye reçinelerdir.

Reçineyle modifiye edilmiş poliüretan sert köpük, içinde kalan solventin uçması için oda şartlarında dört gün bekletilmiştir ve sonra LOI testiyle yanmazlık özelliği incelenmiştir. AA10-CFR, Sep5-CFR ve MM5-AA5-CFR reçinelerinin LOI değerleri CFR'ye gore daha yüksektir, bu sebeple bu reçinelerin poliüretan sert köpüklerde kullanılması köpüğe alev geciktirici etki sağlayacaktır. Ancak TGA ve LOI sonuçları birleştirildiğinde alev geciktirici özelliğin en çok MM5-AA5-CFR nanokompozitinde olduğu görülmektedir.

1. INTRODUCTION

Material science is a valuable discipline that creates new materials and improves products. Metals and ceramics have a significant role in material science; however, it is hard to modify them for various applications. A matter was needed to uplift the comfort of humanity.

A. von Baeyer discovered the oldest synthetic plastic which is phenol formaldehyde resin, however it was Leo Baekeland who convert it into an economical and moldable product. This resin is called as Bakelite at the present time. That was the first polymer that broadly utilized in industry. [1]. Today, humanity lives in polymer age, because whole industry branches use and need polymeric materials. Many materials can be synthesized or modified by utilizing polymers. They can be used as the main material as well as additives. In industry, around seven hundred types of plastics are produced. Since they are light, easily modified, easily moulded and relatively cheap, the demand for polymers is high and it looks like it will be higher with developing new polymer technologies [2].

One of the most versatile polymer in industry is polyurethane. It is developed by Otto Bayer just before World War II and patented by Otto Bayer. After the war, the polyamide production is prohibited and it encouraged the investigations on polyurethane [3].

Rigid polyurethane foams are generally used as insulators to save energy. They are also very durable, resistant to moisture and light. In winter months, heating of buildings would be a serious problem without insulation. In 2000, Public Works and Settlement Ministry of Turkey enacted a law that obligates all buildings to have an insulation coating [4].

A disadvantage of polyurethane foam is high flammability. Higher specific area of polyurethane foam results in high flammability. Since it envelopes the houses, highly flammable polyurethane foam carries risk for human life in case of fire. National building regulations, state and local authorities have specific regulations for

flammability of the polyurethane foams used in constructions. Flame retardants are the additives mixed with foam polyurethane; however, they retard fire or slow down the rate of burning, not prevent it. Flame retardants have high availability; however, there are some obstacles as well. Today, scientists try to develop polyurethane panels that exhibit advanced fire performance properties [5].

In order to increase fire retardance properties of polyurethane, nanocomposites can be applied. In the composite form, the particles, fibers or reinforcing materials have relatively big sizes. Therefore, poor interfacial bonding between bulk polymer and filler happens. However, in the case of polymer nanocomposites, the reinforcing material has nanometer scale. The dispersion of nano material in the polymer matrix is homogeneous [6].

2. THEORETICAL PART

2.1. A Brief Look on Polymer Science

A polymer is a macromolecule composed of many small units that repeat themselves. The small starting molecules are called as monomers and the unit which repeats itself along the chain is called the repeating unit. If the reaction conditions are available, monomers can form covalent bonds with like or unlike molecules in a sequence. Generally, a polymer chain contains thousands of repeat units. The number of repeating unit describes the chain length of the polymer and this number is named as degree of polymerization [7].

A polymer that is consist of a single continuous chain of repeated units is called as linear polymer. If the main chain of the polymer has side chains of repeat units, it is called as branched polymer. A polymer with interconnections between chains is crosslinked polymer. These crosslinks may form during polymerization or after polymerization. Lastly, a crosslinked polymer is a network polymer if it includes numerous interconnections between chain such that the entire material is a single molecule [8].

Solid polymers may be amorphous or crystalline. As the molten form of polymer is cooled down, the molecules are often attracted to each other and packed up as closely as possible by using least potential energy. During the processing of the polymer, if the individual chains are folded in regular form, the polymer becomes crystalline. The chains of crystalline polymers are ordered. However, the chains of amorphous polymers are not ordered, random and even entangled [9].

2.2. Polymer Classification

Polymers are complicated materails and have different properties in contrast to their monomers. Modern day polymers are mostly organic. These organic polymers can be classified according to their sources, thermal behaviour, mechanism of polymerization and properties [10].

2.2.1. Natural and synthetic polymers

Natural polymers are the polymers that form in nature. There are many natural polymers with various characteristic properties. They have been used by people for many purposes and exhibit enhanced compatibility with human hosts, the ability to exhibit bioactivity, and to undergo biodegradation [11]. Enzymes, proteins, natural rubber, DNA and RNA are examples of natural polymers [9].

The polymers synthesized from simple molecules are synthetic polymers. For example, polyethylene, polystyrene, Teflon and PVC [7].

2.2.2. Thermal behaviour of polymers

2.2.2.1. Thermoplastics

Thermoplastics are the materials that soften with heat and harden with cooling.[10,11]. They are linear or slightly branched. As the temperature increases, they soften and flow. They can be molded in soft form and cooled. As the cooling occurs, thermoplastic solidifies and takes the form of mold. They can be reshaped by heat and pressure for various other purposes because no new chemical bond formation occurs during heating and cooling process [7,12]. This cycle can be carried out a few times without affecting chemical properties. Polyethylene, plexiglass, polyvinyl chloride and Teflon are thermoplastics [10].

2.2.2.2. Thermosets

Thermosets are the polymers that become irreversibly hard upon heating with the addition of special chemicals. The hardening is also called as curing, which is a chemical change [10].

Thermoplastic modified thermosets have been investigated to avoid the classical compromises between toughness and thermal stability related with the rubber toughning of thermosets. A new method for increasing toughness of brittle thermoplastic modified thermoset is studied by using triblock copolymers polyphenylene ether (PPE)- and polyetherimide (PEI)-modified epoxy networks [13].

2.2.3. Mechanism of Polymerization

2.2.3.1. Addition polymerization

Rapid self-addition of bifunctional monomers to each other with no elimination of any byproduct is called as addition polymerization. Vinyl monomers, which contain double bonds, goes through addition polymerization [10].

Figure 2.1 : Vinyl Monomer and Vinyl Polymer [10]

Long chains are obtained. By free radical polymerization. π bonds in the carbon-carbon double bonds are susceptible to rearrangement when they are activated by free radical or ionic initiators [14].

A free radical is an atomic or molecular species that contains unpaired electron. It can react with a olefinic monomer to form a chain carrier that is active for a long time as the propagation occurs and macromolecule forms [14].

In addition polymerization, initiator is required. Initiator can be a chemical, heat or radiation. Furthermore, monomer must contain carbon-carbon double bond since the reaction is an alkene addition reaction [15].

PVC, PS, plexiglass and Teflon are synthesized by addition polymerization [7].

Addition polymerization has three steps [14]:

1. Initiation

Initiation is the first step of free radical polymerization. The beginning of this step is decomposition of initiator in the presence of monomer. Double bonds in the monomer create instability. Therefore, monomer is prone to reaction with the unpaired electrons in the radical. The active center of the radical attacks the double bond of the monomer and the addition can happen at either end of the monomer. In a typical synthesis, from 60% to 100% of the free radicals react with monomer in the initiation step. Rest of the free radicals may react with each other or self-destruction can occur [16].

2. Propagation

New free radicals attack other monomers and produce a new free radical in propagation step. In this phase, electron transfer process develops and the resulting movement of the active center results in the generation of polymer. In principle, the propagation step continues as far as the monomer is in the medium, however, this step is repeated until termination occurs, then the reaction finalized [7,16].

3. Termination

It is the last step of addition polymerization. Growing of polymer chain is stopped. Termination can happen in two ways: combination and disproportion. In combination, the free electrons of growing chains find each other and chains combine. In disproportion, a free radical steals a hydrogen atom from an active chain. In the place of missing hydrogen, a double bond is formed and termination occur [7,24].

2.2.3.2. Condensation polymerization

Condensation polymerization is a reaction in which bi-or poly functional monomers go through intermolecular condensation. During the condensation, continuous elimination of byproducts form such as H_2O, HCl, NH_3 and CH_3OH. Condensed matter is generally water. These reactions are catalyzed by acids or alkali. Step polymerization is another name of condensation polymerization, since it occurs rather slowly and stepwise. The molecules at the beginning of the reaction are way much different than molecules at the end of the reaction. Ethylene glycol, terphthalic acid, phenolic resins, nylon and hexamethylene daimine are examples of condensation polymerization [17,7].

In condensation polymerization, polymer chains form slowly. It can take hours to days. The concentration of growing chains is high due to quickly converted oligomers. This type of reaction generally needs high temperatures. Therefore, reaction mixture is heated. In addition, polymers with moderate molecular weight is obtained i.e <100,000. Finally, if a monomer with three or more functional groups is not used, branching and crosslinking does not occur [18].

2.2.4. Properties

2.2.4.1. Elastomers

Elastomers have irregular structure, weak intermolecular attractive forces and very flexible polymer chains. Gross mobility of chains are limited due to the a few crosslinks in the structure, however, they can undergo local mobility. Molecules of elastomers are in coiled shape without tensile strength. Therefore, elastomers show high extensibility, which is up to 1000%. As the applied stress is removed, elastomer recovers and goes back to its original shape. Generally, initial modulus in tension is low, however, elastomers stiffen as they stretched [9].

2.2.4.2. Fibers

Fibers are long, thin and thread like polymers. They do not stretch or go through deformation like elastomers. If the polymer is spun into fibers, the polymer show improved properties. In flexible fibers such as polyester, the chains are relatively relaxed, which means that the chains contain both ordered and disordered parts. Ordered parts give rigidity, while disordered part give flexibility. On the other hand, new rigid fibers have fully extended chains and these chains are parallel to each other, so that strong covalent carbon-carbon bond forms rather than weak van der Walls bonds between long chain molecules. Therefore, molecular structure of polymer and orientation of chains have critical importance in fiber production. As an example, oriented ultrahigh molecular weight polyethylene is a commercial fiber [19,20].

2.2.4.3. Resins

Resin is a solid or pseudosolid organic material with generally high molecular weight that flow when under stress. They generally have softening and melting points and fractures conchoidally. They have wide applications such as consolidants, adhesives, coatings, casting, molding and storage materials. In coating industry, resins are used for glossy appearance. They are resistant to chemicals and adhesion property is excellent. Resins can be obtained from nature or produced by synthetically. Alkyd resins, epoxy resins, polyamide resins, polyurethane resins, vinyl resins, polystyrene resins, acrylic resins are common synthetic resins. They can be classified as thermoplastic or thermoset [21-24].

2.2.4.3.1. Thermoplastic resins

A thermoplastic resin melts with heat and stays molten until it is cooled down. Only the physical change occurs in the solidified polymer [21]. Thermoplastic matrix resins are used in commercial composites especially for high temperature structural applications. Newer thermoplastic resins are based on aromatic polymers, because early aliphatic based resins had low elastic modulus, low glass transition temperature and poor solvent resistance. Now, metallic and fiber reinforced thermosets are being replaced by thermoplastic based components. Thermoplastic resins are advantageous, because they have indefinite shelf life, low moisture absorption and excellent thermal stability, high toughness and damage tolerance [25].

2.2.4.3.2. Thermoset resins

Thermoset resins require curing, so that they form crosslinks. It is irreversible and renders the resin loses the melting ability. It also means that once the resin is cured, it cannot be laminated again except chemical break-down. This development is in progress, especially for polyurethane.

Thermoset resins have high thermal stability, good rigidity resistance to creep and hardness. Uncured resins are generally in the liquid form. By using some other resins, it is possible to partially polymerize the resin and hold it in the B-stage for the production.

Thermoset resins are utilized for binder aims. Special fillers are needed in order to improve mechanical properties, dimensional stability or for flame retardancy. Epoxy resins, phenolic resins, polyester resin, polyimide, silicone are examples of thermoset resins [26].

2.2.5. Plastics

The polymers that can be shaped with heat and pressure is named as plastic. Plexiglass, polyvinyl chloride and teflon are plastics [10].

2.3. Polymerization Techniques

Industrial polymerization techniques can be divided into four classes. The method will be used depends on the nature of the monomer, polymer and polymerization mechanism [7].

2.3.1. Bulk polymerization

Liquid monomers are polymerized by this method. It is a homogeneous system. Monomer, initiator and chain transfer agent is agitated and heated during polymerization. The product has no impurity, just unreacted monomers. No further purification is required. It is an advantageous method due to its simplicity and high conversion rates. However, the heat control is difficult [7].

2.3.2. Solution polymerization

The monomer and initiator are added to a solvent, which is the reaction medium. By using this method, the product is not too viscous, so that mixing and heat control is easier. However, purification and solvent removal is required [12].

2.3.3. Emulsion polymerization

In this method, the reaction occur in aqueous phase. Emulsifier surrounds the growing chain of polymer and form micelles. Initiator is soluble in the aqueous phase. Monomer droplets gets smaller as the polymer micelles gets bigger. However, the produced polymers are very small [12].

2.3.4. Suspension polymerization

Suspension polymerization occurs in a liquid (mostly water) in which monomer is insoluble. Chain transfer agent can be used in order to control the size of chains. Stabilizators are required to prevent sticking of forming polymer particules.In addition, mechanical stirring is required. Initiators are soluble in monomer, not in water. In this type of polymerization, granular form of polymers are produced and filtered [27].

2.4. Cyclohexanone Formaldehyde Resin (CFR)

Ketonic resins are the cyclic ketone condensation products. In 1920s, they are first patented and in 1930s, commercial production of ketonic resins began. Ketone and

aldehydes go through aldol condensation reaction and form ketonic resins. Cyclohexanone-formaldehyde resin (CFR), which has low molecular weight, is a ketonic resin as well. CFR has a good dissolution in both polar and a polar solvent and it is compatible with other polymers as well. Therefore, blending of polymers with CFR is possible. CFR is mostly used in coating and ink industry as it improves weathering resistance, light resistance and filler dispersion in polymer matrix. CFR is also used as a binder in alkyd resin to modify the coating characteristics of alkyd based coatings. CFR has also hydroxyl polarity, so that it results in better wetting of pigments and surfaces. During synthesis of CFR, alkaline catalysis is required. However, it results in corrosion of equipment, tedious separation and it is also harmful for the environment [28,29].

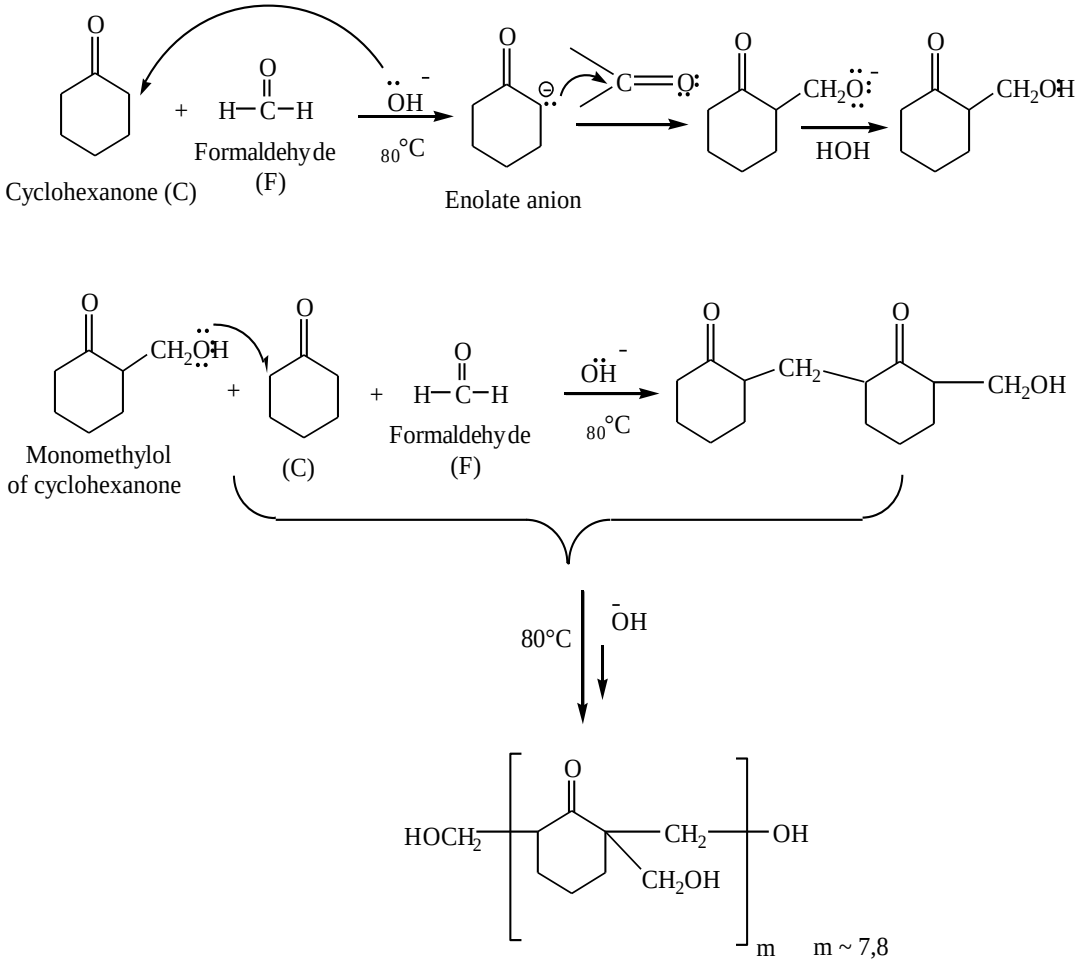


Figure 2.2 : Formation Mechanism of CFR

Ketonic resins can be modified by in-situ by adding reactive compounds into the flask during polymerization of resin. The modifier would react cyclohexanone or formaldehyde. The modifier can be added to the system at the beginning or at the end

of the polymerization. It depends on the reactivity of modifier. Modification of the ketonic resins affects the properties of resins such as solubility and melting point [30-36].

Aldol-like reaction is the starting point CFR formation. Water is eliminated from methylol derivatives of cyclohexanone by introduction of base catalyst. Methylol derivatives of cylohexanones comes together and polymerization occurs [37-40].

In-situ synthesis is an easy and effective way for nanocomposite synthesis. It allows one-step fabrication. By this route, the nanoparticles are grown inside the polymer. It is advantageous, because particle agglomeration is prevented with good spatial distribution of particles in the polymer matrix [41].

In the literature survey, it is observed that CFR resins are investigated for many purposes. Firstly, CFR is blended with palm stearin/dehydrated castor oil and palm stearin/linseed oil alkyd resins to improve the virgin alkyd resin. Due to limited petroleum resources and high oil prices, a vegetable oil that is palm oil is used for alkyd resin synthesis. This resin is blended with CFR and air drying time, hardness, adhesion, gloss, impact strength, chemical resistance and thermal behavior of dried films of blends are measured. It is concluded that CFR addition improved physical, chemical and mechanical properties of alkyd resin. The best result is obtained as 70% alkyd resin is mixed with 30% CFR in weight [29].

CFR can be modified with clay. Montmorillonite and polydimethylsiloxane with diamine chain ends can be used to increase the thermal stability of CFR. The formed resin has layered structure confirmed by XRD results. DSC and TGA results showed that thermal stability of CFR can be increased by addition of clay [42].

Conductive CFR can be obtained by in situ modification. Aniline and 4-aminodiphenylamine andN-N'-diphenyl-1,4-phenylene diamine are used for in situ modification of CFR in presence of sodium hydroxide. With aniline, dimer and trimer aniline addition to the system, conductive CFR with 10-3-10-5 S/cm conductivity is obtained. CFR with aniline group may provide the adhesive strength of a coating and it may act like a corrosion inhibitor to metal surfaces. This study showed that application of conducting resins is possible [43].

For good adhesion property of CFR on plexiglass, CFR and methylmethacrylate can be synthesized as block-graft copolymer. They are prepared via atom transfer radical

polymerization(ATRP). Hydroxyl groups of CFR are modified with 2-bromopropionyl bromide. In the ATRP of MMA, copper bromide (CuBr) is used and N,N,N′,N″,N″-pentamethyl-diethylenetriamine (PMDETA) as catalyst at 90°C [44].

Cyclohexanone formaldehyde is also modified with melamine, recorcinol, p-toluene sulfonamide, bisphenol-A and bisphenol-C. Solubility of the modified resin depends on the type of the resin. For example, melamine and bisphenol-A modifed CFR has better solubility in ethanol and acetone than unmodified CFR, however, bisphenol-C modified C has low solubility in almost all solvents. Also, it is concluded that modifier attached to the base resin, probably on the methylene bridges [45].

UV-curable cyclohexanone-formaldehyde (UVCF) resin can be synthesized by adding isophorone as a base substance, diisocyanate (IPDI) as bridging agent and pentaerythritol triacrylate (PETA) as the functional monomer. The photopolymerization conversion is more than 80% if the UV irradiation time is 230s. Thermal stability of the UVCFR is good since crosslinking occured in the resin. When UVCF content is 60% , UVCF showed good mechanical properties [46].

2.5. Polyurethane

Polyurethanes are any type of polymer containing a -NH-CO-O-, which is called as urethane linkage. Polyurethane is synthesized by the reaction of isocyanates and polyols to have an active hydrogen, such as diols, which contains hydroxyl groups. The reaction is exothermic. During the reaction, viscosity and temperature increases. Polyurethanes are produced by bulk or solution polymerization. Since bulk polymerization is environment-friendly, it is more preferable in industrial scale. On the other hand, in the laboratory, solution polymerization is more preferable [47,48].

Polyurethane can be produced by both condensation polymerization reaction of bischloroformates with diamine and addition polymerization reaction of diisocyanates with di or polyfunctional hydroxy compounds. In the second route, no byproduct is formed [49].

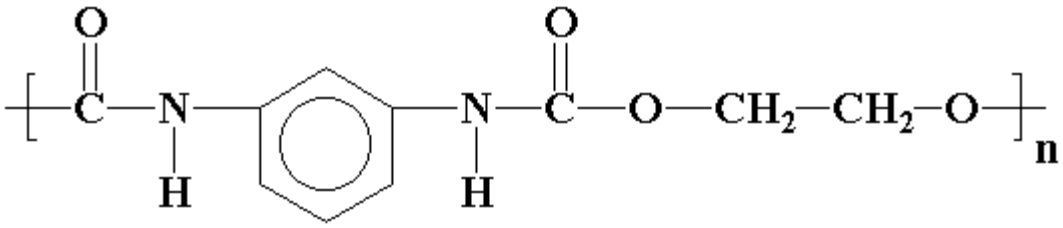


Figure 2.3 : Polyurethane Structure

While there are thermoplastic polyurethanes in market, most of the polyurethanes are thermosets. Therefore, unrecyclable nature of thermoset polyurethane is an disadvantage. While the chains of thermoplastic polyurethanes are linear and they are packed in mostly crystalline form, thermoset polyurethanes have cross-linked. In addition, polyurethanes have amber color and can be stretched easily. They are resistant to scratch, impact and tear. They are also resistant to organic solvents, acids and oils [47,50].

Polyurethanes are block copolymers with hard and soft segments. Soft segments are formed by poliols. These segments provide elasticity to foam. Diizosyanates are responsible for hard segments and provide mechanical properties [48].

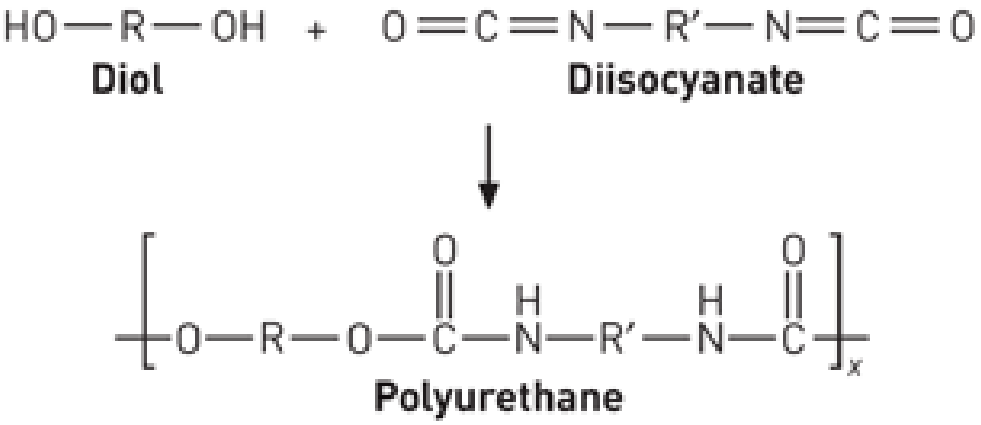


Figure 2.4 : Polyurethane Synthesis by Diol and Diisocyanate

Phase separation occurs due to chemical and thermodynamic difference of soft and hard segments. The degree of phase separation is based on hydrogen bonds, polarity and the length of the segments. The phase distribution of hard and soft segments can be modified in order to change the mechanical, physical and biocompability properties of polyurethane [48].

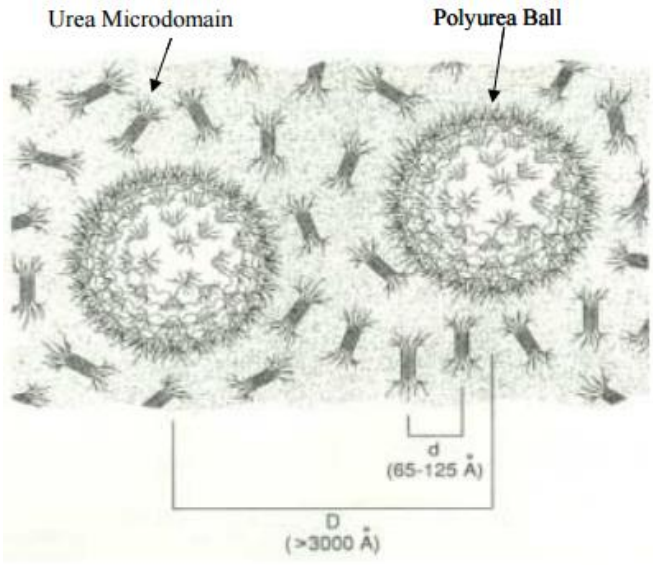


Figure 2.5 : Phase Separation of Polyurethane [51]

2.6. Polyurethane Foams

There are many kind of polyurethane foam in industry, because many compounds include active hydrogens and various kinds of diisocyanates can be utilized for foam polyurethane production. Polyurethane foam can be in two forms: flexible or rigid foam. They are used as coating and adhesive materials. While flexible polyurethane foams are utilized for cushioning and packaging, rigid polyurethane foam is applied in insulation, adhesive, transportation and floatation industry. For example, Rhinoskin is sprayed on the surface of materials and it forms a protective layer for the material [47].

Figure 2.6 : Polyurethane Foam

Rigid polyurethanes foams are different than flexible polyurethane foam in cellular structure. The cells of rigid polyurethane foam are almost fully closed. It results in low flexibility, high load bearing capacity and high thermal insulation property. Cells of rigid PU foams are formed by liquid physical agent or pressurized air, while water

is used in thermoplastic PU foam as blowing agent. Ozono depletion potential CFC and HCFC are now replaced with new-generation blowing agents, which is a breakthrough in rigid PU foam production. They are HFC blowing agents, especially HFC-245fa [52].

The reason that rigid polyurethane foam is used in insulation area is better thermal properties of rigid polyurethane than thermoplastic foams. Their low conductivity is due to blowing agent properties, cell size and closed cell morphology. The blowing agent is 95-97% of the foam volume and contributes 50-70% to the overall foam conductivity. However, insulation performance of rigid performance lowers with time, because blowing agents diffuses out of the cells and the cells are filled with air.

Rigid PU foams are generally produced in the form of blocks and sheets in which lamination technology is used for the production. The mixture is poured down in a mold or sprayed. A storage tank, metering pump, mixer and a final forming device is required for rigid PU production. Since CFC blowing agents are replaced with new generation highly flammable blowing agents, caution must be taken to prevent flammable vapor emissions [52].

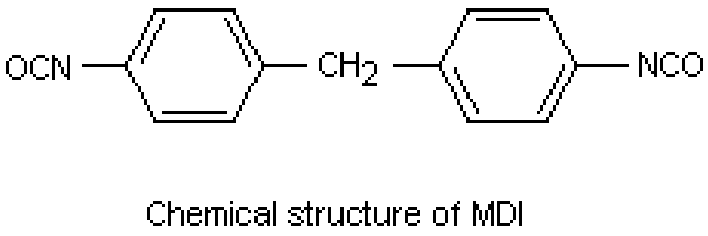
By using green technology, PU foam can be modified to improve foam's properties by integration of organic nanoclay into the foam. Modified diaminopropane montmorillonite (DAP-MMT) nanoclay can be added to palm oil based polyol. The produced foam is exfoliated and intercalated in structure. By using this technique, compressive strength and thermal stability of foam can be improved. DAP-MMT is reduced the size simultaneously with no change of chemical structure. Agglomerated DAP-MMT particules act as a barrier and protect the foam from degradation [53].

Polyurethane foams can be modified with microsphere and nanoclay fillers. In a study, these modified foams, which contain oil based polyol, are compared with 100% petroleum polyol. It is found that at 7% of microsphere filler addition, the compressive strength of foam is the same with the one made from 100% petroleum polyol. Compressive strength of nanoclay filler added PU foam decreased due to weaker matrix structure at 7% filler addition. Therefore, optimized filler percentages are 5 to 7% microspheres or 3 to 7% nanoclay, because compressive strengths are comparable or superior to the one with 100% petroleum polyol. In addition, microsphere and nanoclay fillers result in more cells with smaller cell sizes. Foams

with fillers displayed roughly the same thermal conductivity as soy-polyol based foams without fillers [54].

2.7. Isocyanates

Isocyanates are used in elastomers of automobile bumpers, shoe soles, spandex fibers and printing roll. They, containing –N=C=O group, are very reactive chemicals due to their chemical configuration. They react with active hydrogen in compounds such as water, acid and alcohols. They also react with each other and form dimer. Toluene diisocyanate (TDI), a combination of 2,4-TDI and 2,6-TDI, was a highly used isocyanate for foam PU production. However, Methylene diphenyl diisocyanate (MDI) has replaced TDI since it is less hazardous than [55].



Chemical structure of MDI

Figure 2.7 : MDI [56]

In polyurethane foam production, isocyanate is mixed with polyeter or polyester polyols with addition of combustion retarding agents, catalyst and blowing agents. If the water is added, it results in foam formation with generation carbondioxide. However, isocyanates affect human health negatively. It damages mostly lungs with other organs as well. The most reported toxic isocyanate is toluene diisocyanate due to its widespread usage [55].

Isocyanates react with water, so that amines and carbondioxide formation occurs. The reaction of isocyanite and water produces thermally unstable carbamic acid that decomposes and produces amine functionality, carbon dioxide and heat. In the newly formed amine group reacts with another isocyanate group to give a disubstituted urea and additional heat is generated [57].

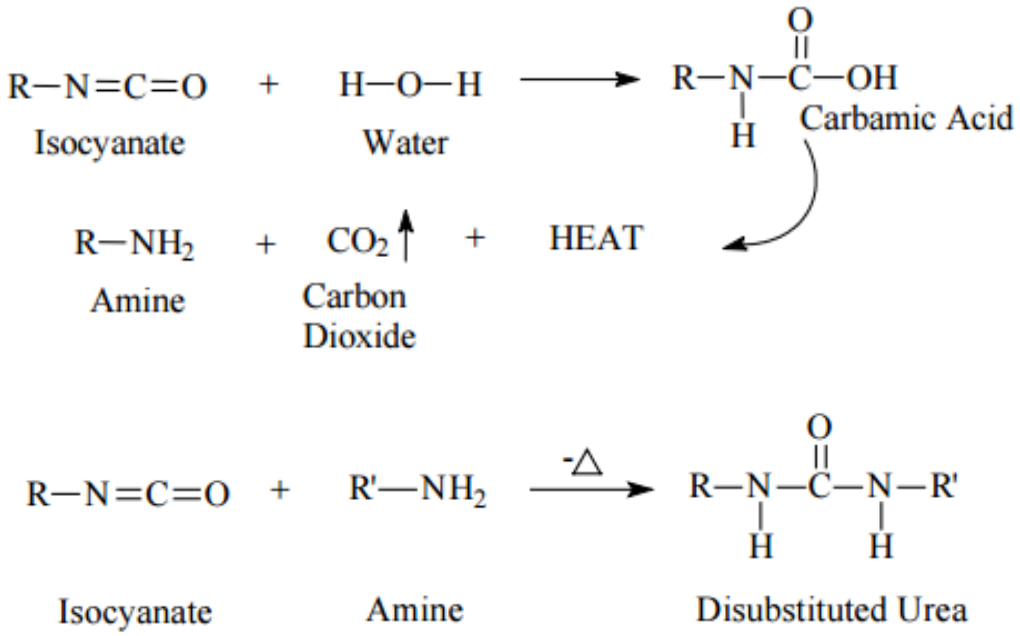


Figure 2.8 : Isocyanate Reaction With Water [58]

Aliphatic isocyanates have lower reactivity than aromatic isocyanates. If metallic catalyst such as tin, lead, zinc or iron are used, the reactivity of aliphatic isocyanates can be increased. On the other hand, aromatic isocyanates are not stable to light and get yellowish color with time [48].

2.8. Polyols

The sources of the polyol are plants, oil or wood. Castor, soybean or rapeseed can be used for polyol production as well. As a renewable source, vegetable oils are good alternative sources, because they are compatible with hydrocarbon blowing agents, they have higher hydrophobicity and high hydrolytic properties. Produced PU foam has good oxidative stability as well [59].

There are various kind of polyols based on chemical structure, molecular weight, and functionality. However, especially two types of polyol are used mostly for foam PU production, which are polyether and polyester polyols. 90% of four billion pounds of polyurethanes consumed in the United States was synthesized from polyether polyols, 9 % on polyesters and 1% on other specialty polymers [60].

Polyether polyols used for rigid polyurethane foam production are obtained by the polyaddition of PO and/or ethylene oxide to high functionality polyols having 3–8

hydroxyl groups/mol. The chain derived from one hydroxyl group have maximum 1-3 PO units. A usual procedure for making polyether polyols is alkoxylation of a mixture of two polyols such as: glycerol–sorbitol, glycerol–sucrose, dipropylene glycol–sorbitol, diethylene glycol–sucrose with PO [61].

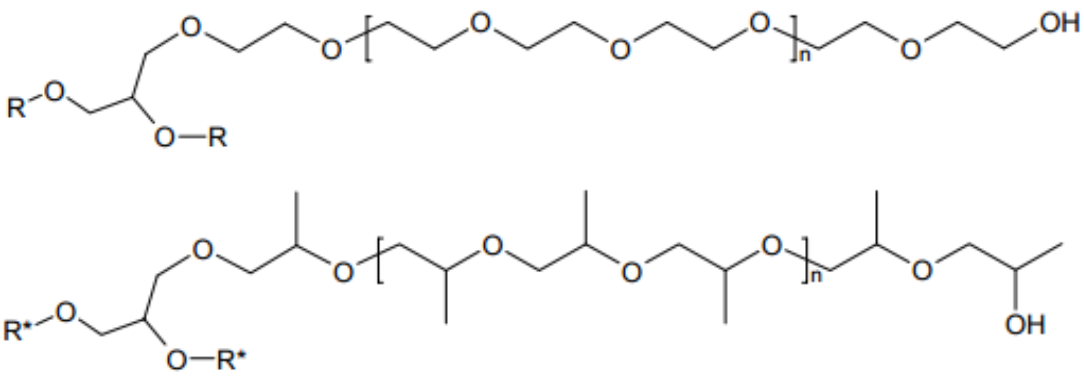


Figure 2.9 : Polyether Polyols Made From Ethylene Oxide (Top) and Propylene Oxide (Bottom) [62]

Polyester polyol that are derived from aliphatic and aromatic dicarboxylic acids are important for polyol industry. Glycols such as 1,6 hexanediol or polyols such as glycerin react with diester or diacid and produce primary polyester polyols. Low-molecular weight oligomeric derivatives of phthalic and terephthalic acids are utilized in high strength and rigidity polyesters. They provide a lot of advantages like including good mechanical characteristics, high thermal stability, resistance to major chemical solvents, and low flammability. Polyester polyols can be synthesized from terephthalic acid with glycols at above 220°C. During this process, esterification reactions occur. Water is formed and ester links are hydrolyzed [60,63].

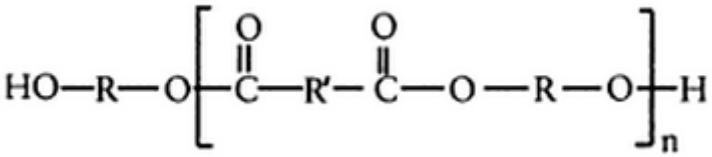


Figure 2.10 : Polyester Polyol [64]

Polyol selection is based on the application area of final product. For example, if hydrolytic stability and heat resistance is required, polyeter polyol should be chosen.

If solvent resistance and superior physical properties is required, polyester polyol should be chosen [48].

2.9. Polymer-Clay Nanocomposites

2.9.1. Nanocomposites

Polymer nanocomposites are two-phase materials, in which the polymers are reinforced by nanoscale fillers [65]. It is one of the most popular area for all disciplines to research such as microelectronics, polymer based biomaterials, nanoparticle drug delivery, miniemulsion particles, fuel cell electrode polymer bound catalysts, layer-by-layer self-assembled polymer films, electrospun nanofibers or imprint lithography. Nanocomposites application can be done for reinforcement, barrier properties, flame resistance, electro-optical properties, cosmetic applications, bactericidal properties [66].

The structure and final properties of nanocomposites depends on the degree of the dispersion of the clay particles into the polymer matrix. Nature of the components (layered silicate, organic cation and polymer matrix) and method of preparation results in three main types of composites as the layered clay is associated with a polymer.

i.Non mixing composites: the interactions between polymer and clay are very weak. Therefore the polymer cannot migrate into the clay layers. A separated layer is formed and mechanical properties are not satisfactory.

ii. Intercalated structures: These structures have a well ordered morphology since polymer chains intercalated between the clay layers, which creates 2-3 nm distance between layers. It is independent of the clay to polymer ratio. These type of nanocomposites are similar to ceramic materials.

iii. Exfoliated or delaminated structures: ın this case, the clay layers are fully separated and well dispersed in the polymer matrix. The distance between layers is between 5-10 nm or even more. The clay-polymer interaction is maximum, therefore mechanical and physical properties are improved. It is known that exfoliated structures have better mechanical properties than intercalated structures [65].

Final properties of nanocomposites depend on four main components:

i. The filler aspect ratio

ii.The filler dispersion

iii.The filler alignment and orientation

iv.The polymer-polymer and polymer-filler interfacial interactions

X-Ray Diffraction is a method that is utilized for determination of the nanocomposite structure. It is also used for kinetics of the polymer melt. The structure can be intercalated or exfoliated. It is characterized by the position, shape, and intensity of the basal reflections of the distributed layers of the sample nanocomposite [65].

In an exfoliated nanocomposite, the extensive layer separation along with the delamination of the silicate layers in the polymer matrix leads to disappearance of coherent X-ray diffraction of the distributed silicate layers. In addition, the finite layer expansion of intercalated nanocomposites along with polymer intercalation leads to the appearance of a new basal reflection corresponding to the larger gallery height [67].

2.9.2. Methods for the nanocomposite synthesis

Nanacomposites can be produced by four general methods [68].

2.9.2.1. Template synthesis

Inorganic material is synthesised in the presence of polymer matrix. Nucleation and growth of the inorganic crystals occurs and polymer forms in the layers. By using template synthesis method, exfoliated nanocomposites can be produced, however, use of high temperature and tendency of the generated filler to aggregate are disadvantage of this method. Therefore, it is not widely used [68].

2.9.2.2. Intercalation of polymer from solution

In this method, organically modified silicate is dispersed in a solvent and the polymer is also soluble in this solvent. As the solvent is evaporated, the polymer is absorbed onto the sheets and an ordered multilayer structure is obtained. This method is generally used for the intercalation of the water - soluble polymers like poly(vinyl alcohol), poly(ethylene oxide), poly(acrylic acid), poly(vinlypyrrolidone),etc. In the process of intercalation, the entropy of polymer chains decreases and it is compensated by the increase in the entropy of the solvent molecules due to their

desorption from the filler interlayers. This technique is also be used in organic solvents for polymers insoluble in water [68].

2.9.2.3. Melt intercalation

This method and in-situ polymerization methods are generally used in industry for nanocomposite production. In melt intercalation, layered silicate is blended with polymer matrix in the molten state. A compatible polymer with layered silicate can fill the interlayer space of clay and form either an intercalated or an exfoliated nanocomposite [69].

The blending occurs at high temperatures and the filler is blended with polymer melt under shear. No chemical synthesis or solvents are required. However, the intercalation of high molecular weight polymer chains in the filler interlayer is hard thermodynamically. For that reason, the filler is modified in a way that it can be exfoliated in the polymer matrix by the action of shear. In addition, low molecular weight organic or inorganic compatibilizers can be added to the system for his purpose [68].

Since the system is at high temperature, thermal degradation of the filler modification and polymer is a concern. Even a small extent of degradation can affect the filler matrix interactions and hence affecting the microstructure of the composites [68].

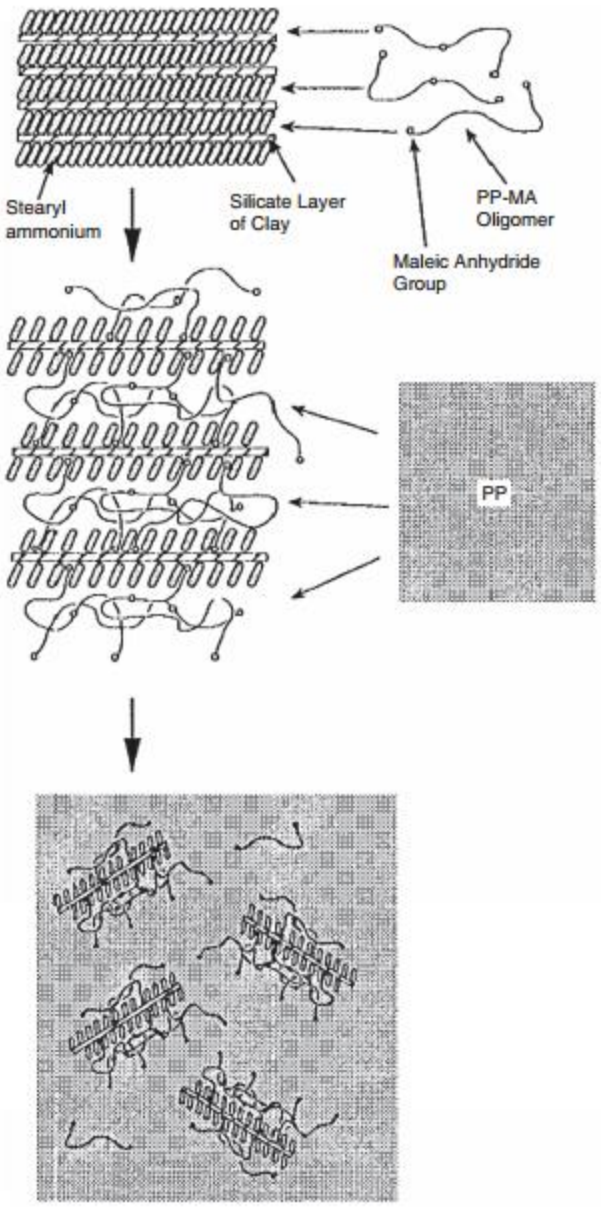


Figure 2.11 : Melt Intercalation in which modified filler was first mixed with compatibilizer, followed by the compounding of this hybrid with polymer [68]

2.9.2.4. In - situ synthesis

It is the first method for synthesis of polymer–clay nanocomposites based on polyamide. This research was conducted by Toyoto workers and it resulted in an exponential growth in nanocomposite technology. In in-situ polymerization, the modified layered silicate is swollen by a liquid monomer or monomer solution. The monomer fills the gap between layers of silicate and polymerization occurs in these layers. As the polymerization occurs, intercalation or exfoliation occurs in the sheets as well [68,69].

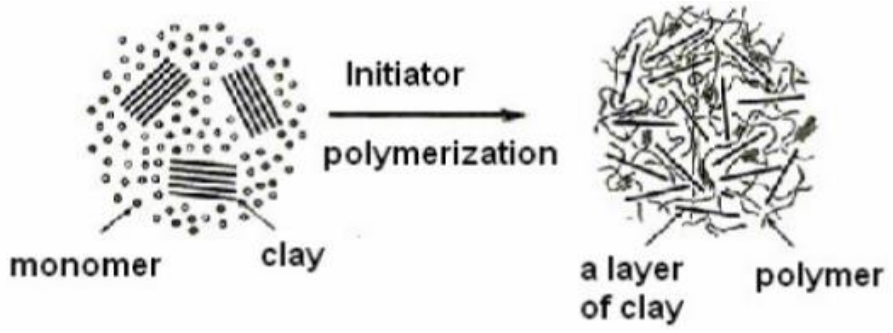


Figure 2.12 : In Situ Polymerization

The advantages of in situ polymerization are one step synthesis of the metallocene polymer nanocomposites, improved compatibility of the clay and the polymer matrix and enhanced clay dispersity [70].

Long chain polymers are produced in the clay galleries. If intra- and extra-gallery polymerization rates are totally balanced, the clay layers are delaminated and the product obtains a disordered structure. Therefore, controlling of polymerization rates in intragallery and extragallery are highly important. Heat or radiation, a suitable initiator or an organic initiator or catalyst fixed through cationic exchange inside the interlayer can be used for initiation [68,69].

2.9.3. Studies on resins produced by In-situ polymerization

Epoxy resins, which are used in electronics for their excellent thermal, mechanical and electronic properties, can be modified with in situ polymerized thermoplastic polymers in order to obtain high toughness and heat resistance of the resin. The monomers of the thermoplastics are added to the epoxy resin and thermoplastic resin are formed during the curing of the resin with in situ polymerization. By this method, the cured resin is modified and semi interpenetrating polymer network that blends two polymers by entangling the molecular chain of thermoplastic polymer to an epoxy network without forming chemical bonds. With this method, a homogenous blend of resin matrix and thermoplastic polymer are obtained. At the end, by radical polymerization, a thermoplastic polymer is formed during the curing of epoxy resin with higher glass transition temperature and higher toughness [71].

In situ polymerization also attracted the composite optical resin researchers. Scientists produced transparent optical resins containing terbium complexes by in situ polymerization. They are also produced this composite with europium by free

radical polymerization. Composite resins with narrow bandwidth and intense fluorescence are obtained by using methacrylic acid (MA), styrene (St), $EuCl_3 \cdot 6H_2O$, and organic ligands. With in situ method, binary or ternary Eu^{3+} lanthanide ion complexes are produced. It is concluded that the composite resin produced by the in situ method indicated stronger emission intensities and longer lifetimes than the optical resins produced by the doping method with the same lanthanide content. It TEM results also indicated that the lanthanide complexes, with a mean diameter below 20 nm, were homogeneously dispersed throughout the composite resins [72].

In situ polymerization is also used for preparation of Montmorillonite–phenolic resin nanocomposites. Montmorillonite-resol and Montmorillonite–novolac nanocomposites were prepared by one-step in-situ intercalative polymerisation with the modification of quaternary ammonium salts. By XRD and TEM tests, it is known that montmorillonite layers were more easily exfoliated or intercalated in novolac than in resol due to the linear structure of the novolac, which facilitates the intercalation between the montmorillonite layers. One-step in-situ intercalative polymerization is used for production of montmorillonite–phenolic resin nanocomposites. Intercalation and polymerization proceed simultaneously and it resulted in intercalated CPN. In this study, it is concluded that the intercalation was higher in the montmorillonite–resol nanocomposites and with the cetyl trimethylammonium bromide modified montmorillonite. Lower glass transition temperature is obtained due to the influence of montmorillonite on the polymerization process, which resulted in changes in the molecular structure of the novolac resin, an increased content of p–p linkages and a of the resin [73].

A new acid-based composite membrane is obtained by in situ polymerization. PBI oligomer and TMBP in SPEEK membrane formed a semi-interpenetrating polymer network in situ. A cross-linking reaction between PBI oligomer and TMBP and the acid–base interaction between sulfonic acid groups and benzimidazole groups occured and created three-dimensional network structure. water uptake, swelling ration and methanol permeability compared with pristine SPEEK of the composite membranes are drastically reduced. Thermal and oxidative stability, mechanical properties and proton conductivity were significantly improved. At the end, in situ polymerization was shown efficient for the DMFCs membranes [74].

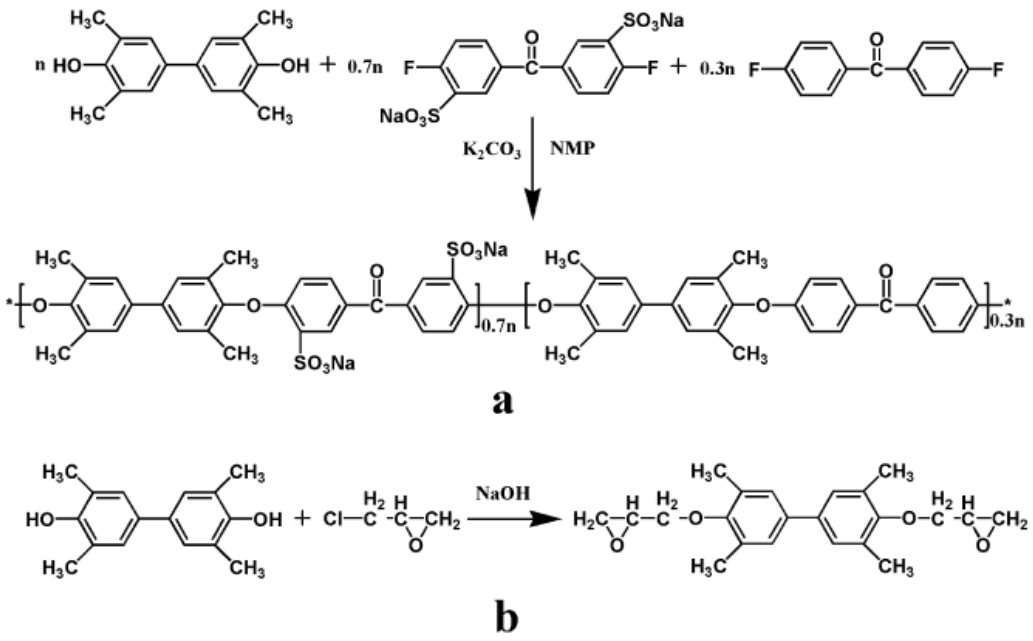


Figure 2.13 : The Preparation and Chemical Structure of SPEEK and TMBP [74]

In situ bulk polymerization can also be used for synthesis of high impact resins. It results in considerable reduction of costs because of its simplicity of the process. ABS, which is acrylonitrile–butadiene–styrene copolymer, is rubber-toughened thermoplastic that displays several attractive properties, such as impact toughness, solvent resistance and good processability [75]. In a study, ABS resin is prepared through in situ polymerization. . Nd(P507)3/Al(i-Bu)2H/Et3Al2Cl3 catalyst was employed for the selective polymerization of butadiene in styrene to produce butadiene prepolymer solution and the produced prepolymer solution was directly used for the synthesis of ABS resin. The study showed that the impact strength increased with the increase of polybutadiene content. Higher impact strength is obtained with the ABS toughened by prepolymer with broad Mw/Mn [76].

The synthesis of polymer coated core–shell microcapsules are produced by in a in situ polymerization industrially. In the in situ polymerization, monomer intercalation is followed by polymerization and it facilitates high coverage and shell strength, because polymerization occurs on the surface of core material instead of a simple dissolution/precipitation physical process. In a study, melamine–formaldehyde resins were selected for the fabrication of nitramine explosives that are cyclotrimethylenetrinitramine-RDX, cyclotetramethylenetetranitramine-HMX and hexanitrohexaazaisowurtzitane-CL-20 based microcapsules, the polymer coating

shell prepared by in situ polymerization of melamine and formaldehyde on the surface of explosive crystals. As the prepolymers of MF resins are prepared, the polymerization reaction was started after sufficient intermolecular interactions among explosives and prepolymers formed. SEM and XPS results showed that a well coating of MF resins with high surface coverage, reduced impact sensitivity of such energetic microcapsules and improved thermal stability are obtained [77].

2.9.4. Montmorillonite

The source of montmorillonite is bentonite. It is a rock having highly colloidal and plastic clays mostly composed of montmorillonite. They are able to replace the exchangeble cations by other organic or other metal cations in solution. Montmorillonite is in the class of smectites. It has layered structure. Every structure consists of two tetrahedral and one octohedral structure the width is generally 10 Å. Montmorillonites, which are layered silicates, are used in nanocomposites and comes from natural or synthetic minerals. They consist of very thin layers that are bound together with counter-ions. When the ions between crystal structure has a different alignment, negative charge forms between layers. There are cations such as Ca2+, Na+ in order to balance the negative charges. The characteristic properties of montmorillonite is that the cations can be changed with other cations. The silicon of the tetrahedral sheets are surrounded with by four oxygen atoms and octahedral sheets in which a metal like aluminum is surrounded by eight oxygen atoms. In 1:1 layered structures such as kaolinite, a tetrahedral sheet is fused with an octahedral sheet and the oxygen atoms are shared. [78,79,80].

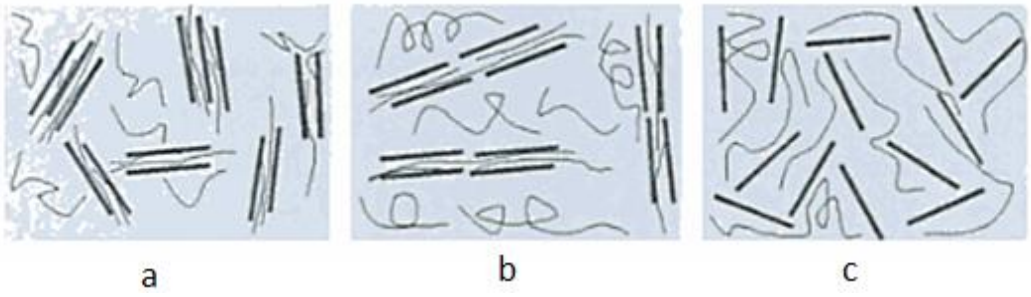


Figure 2.14 : (a)Intercalated, (b) Intercalated and Flocculated and (c) Exfoluated Structure [81]

Clay minerals in the class of bentonite show thixotropic-gel formation with water. They have high water absorption, and high cation-exchange capacity, however,

these properties depend on the nature of interstitial water and exchangeable cations in the interlayer space. Montmorillonite is highly used in polymer nanocomposites since they have potentially high-aspect ratio and high-surface area. Their presence enhance the polymer properties hugely and they are also environmentally friendly, naturally occurring, and readily available in nature. However, agglomeration can be a problem since the layered silicates in their pristine state are hydrophilic; the nanolayers are not easily dispersed in most polymers. Layered silicates should be organically modified to produce well-organized nanocomposites, because dispersion of the inorganic platelets into discrete monolayers is concealed by the intrinsic

incompatibility of hydrophilic layered silicates and hydrophobic engineering plastics.

Furthermore, montmorillonite can form stable suspensions in water because its hydrophilic character also enhances the dispersion of inorganic crystalline layers in water soluble polymers, such as polyvinyl alcohol and polyethylene oxide [75].

2:1 structure is a basic structure with silicon in the tetrahedral sheets and aluminum in the octahedral sheet, without any substitution of atoms. This structure is called as pyrophyllite. Pyrophyllite has no internal area, but external area. As silicon in the tetrahedral sheet is filled by aluminum, the structure is called as mica. This mineral has negative charge and it is balances by interlayer potassium cations. he hexagonal hole created by the Si/Al tetrahedral layer is perfect for the size of the potassium ions. They can fit very tightly between layers. Therefore, the layers are held together by electrostatic attraction between the negatively charged tetrahedral layer and the potassium cations. However, the structure of montmorillonite is formed, if in the original pyrophyllite structure the trivalent Al-cation in the octahedral layer is partially substituted by the divalent Mg-cation. [82].

Montmorillanite can be used to give barrier properties to polymers by the addition of montmorillanite to polymer with sufficient aspect ratio to alter the diffusion path of gas-penetrant molecules. For this aim, effective dispersion of montmorillanite and exfoliation of the platelets into the polymer matrix must be done to get a tortuous diffusion pathway for improved barrier properties [83].

In a study, montmorillonite is used in polypropylene in order to enhance the mechanical properties. 6 wt % of polypropylene is used as montmorillonite. In the preparation of the nanocomposite, two routes are followed: either by using

functionalized polypropylenes and common organo-montmorillonites, or by using neat/ unmodified polypropylene and a semi-fluorinated organic modification for the silicates. This polypropylene and montmorillonite nanocomposite resulted in coexisting intercalated and exfoliated structure. At the end of the study, tensile characteristics are improved and higher heat deflection temperature, high barrier properties, better scratch resistance, and increased flame retardancy are obtained [84].

Even if montmorillonite is used at very low concentrations such as 1-5%, Polymer/Montmorillonite nanocomposites generally improve the properties of polymers opposed to the traditional advanced composites, which requires high volume fraction of clay i.e >50% [42,85].

2.9.5. Sepiolite

Sepiolite is a clay mineral, which belongs to the phyllosilicates class of clays is a hydrated magnesium silicate clay. It has various advantageous properties such as white color, low specific gravity, high absorption capacity, chemical composition and low thermal conductivity [86,87].

Sepiolite can be found in different forms in various countries. For example, sepiolite in the form of lumps is extracted from Eskişehir, Turkey. Sedimentary bed form of sepiolite occurs in Amboschi, Tanganyika, matted plates (mountain leather) or fibers of sepiolite occur in Ampandrandava, Madagascar. These various structures of sepiolite are based on long single crystal fibers that have thicknesses of only 100/~ to several hundred A. Aggregation of these forms are due to the felting in one, two, or three dimensions of these extremely thin single crystal fibers [88].

Sepiolite structure is determined by Brauner and Preisinger (1956). The ideal formula of the sepiolite [88]:

$$1(H_2O)_n.1\{Mg_8(H_2O)_4(OH)_4[Si_{12}O_{30}]\}\ ;\quad n\leq 8$$

The unit cell characteristics are:

a=13.4 Å, b=26.8 Å, c=5.28 Å, Z = 2 P- D_{2h}^{6}

Sepiolite has needle-like structure. These kind of clays shows a hole diameter of 0.3-0.6 nm, a cross section of 20-50 nm, a length of 1.5-2 μm [89].

Sepiolite is a phyllosilicate and contains a continuous two-dimensional tetrahedral sheet. It is different from layer silicates, because it lacks continuous octahedral sheets. The structure of sepiolite contains ribbons of a 2:1 phyllosilicate structure. These ribbons are linked to the next by inversion of SiO_4 tetrahedra along a set of Si-O-Si bonds. At each inversion of tetrahedra, an octahedral sheet is discontinuous. Oxygen atoms in the octahedra at the edge of the ribbons are interconnected to cations on the ribbon side only. Charge balance and coordinations happen along the channel by protons, coordinated water and a small number of exchangeable cations. The channels also contain water [90].

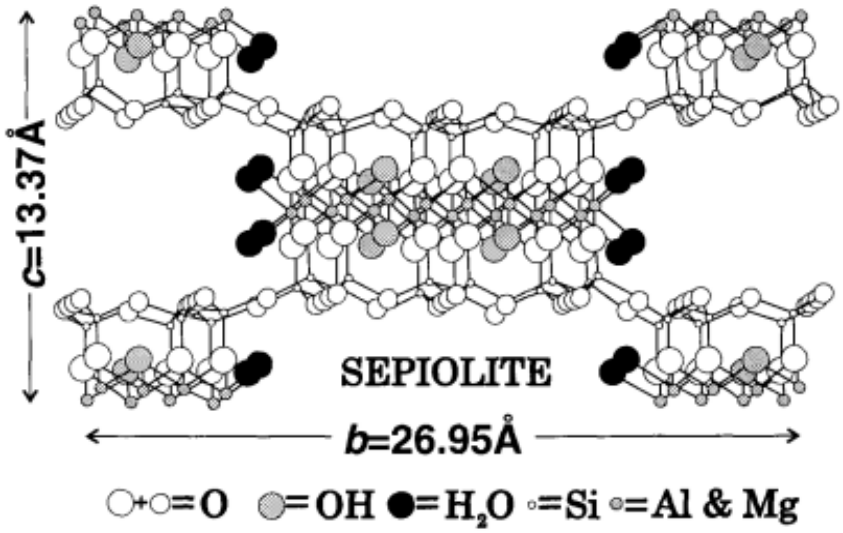


Figure 2.15 : Structure of Sepiolite [91]

The channels in the sepiolite increases the specific surface area of these particles up to 200–300 m2/g. Using this property, it is used in rheological, sorptive and catalytic applications [92].

Sepiolite clay has wide range of application. The first one is absorbents. Sepiolite is used in cat litter absorbents, pesticide and herbicide carriers and bleaching agents for mineral and vegetable oils, paraffins, fats, butter and wine. Secondly, catalyst carriers contains sepiolite. The catalytic activity of sepiolite is due to silanol groups present on the surface . It is a little bit acidic, therefore, The catalytic activity of clays is primarily a function of their surface activity act as catalysts at reaction sites . sepiolite is also used as organo-mineral derivative. Rheological application is another area of sepiolite usage, which involves thickening, gelling, stabilizing or other modification of their rheological properties. sepiolite is utilized as reinforcing filler

in rubbers and plastics as well. It is used in paints, adhesives, sealants , fertilizer suspensions and cosmetics. Sepiolite has also been investigated for application of animal nutrition due to its free-flowing, anti-caking, and non-toxic properties [90].

In a study, the effects of sepiolite modified with g-aminopropyltriethoxylsilane on thermal properties of polyurethane nanocomposites were investigated. It is observed that sepiolite increased the glass transition temperature of hard segments of the composite increased, because sepiolite limits the hydrogen bonding formations. It is also concluded that sepiolite delayed the thermal decomposition of pure polyurethane. Tensile properties are determined after aging is applied and it is observed that the percentage loss in tensile strength decreased due to oxidation barrier that sepiolite formed [96].

The effects of polymers, which are PVA and polyurethane, on the dispersion properties of sepiolite is an investigation topic as well. The added polymers to the clay interact with clay particles, depending on their ionic or non-ionic character. Rheological properties, mineral structure and content is used for determination of sepiolite dispersion. It is observed that polymer molecules cover the surface of sepiolite particles and changed the flow properties of the dispersions as stable dispersions at some certain concentrations. Polyurethane covered the surface of sepiolite faster than PVA. However, PVA covered the surface more smoothly. Thermal properties improved by both, while PVA is more successful than polyurethane. These polymers can be used for modification of the flow and the surface properties of the sepiolite particles and it is possible to produce stable dispersions with PVA and polyurethane [97].

2.10. Alendronic Acid

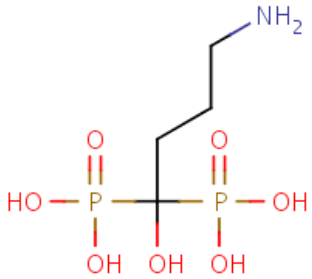


Figure 2.16 : Alendronic Acid [93]

Alendronic acid is mainly used in medicine industry for a disease treatment named osteoporosis. This illness affects the bone and results in low bone mass. The bone gets more fragile and fracture risk is high. Bisphosponates, which is alendronic acid, is used in treatment of osteoporosis despite their low bioavailability and some side effects. Alendronate sodium is a bisphosphonate and has low oral bioavailabilty. This is a problem for patients, so that more soluble salt alendronate sodium should be used rather than insoluble form of alendronic acid [94].

Alendronic acid can also be used for flame retardancy properties. Bromine containing flame retardants, such as g brominated diphenyl oxide flame retardants, was being used as flame retardants until they are banned due to toxicity. As an alternative, phosphorus containing flame retardants are proposed. They are more preferable than halogen containing flame retardants due to low toxicity, less release of toxic gases and slow formation of smoke in the case of fire. Phosphorus begins to act as a fire retardant in the condensed phase. Phosphorus compounds decompose as the heat exposure occurs. As the product of the reaction, phosphoric or polyphosphoric acids forms and they catalyzes the formation of phosphorus-rich char in the condensed phase. If alendronic acid is used for flame retardancy of polyurethane, phosphoric acid reacts efficiently with carbomiimide that is formed by condensation of isocyanate. Carbonaceous char forms and it prevents the heat transfer to the foam surface. Nitrogen containing flame retardants, which are good alternative for alendronic acid, can be used for synergistical effect for flame retardancy [95].

Fire resistance of rigid polyurethane foam can be increased by addition of phosphorous containing flame retardants. By addition of the flame retardant to rigid polyurethane foam, better compressive strength, thermal stability, char residue, heat release and smoke emission can be obtained. Reinforced char layer forms after combustıon and it develops flame resistance to the foam [95].

2.11. Fire Retardancy

2.11.1. Overview of fire and fire retardants

The industry is working actively to solve the flammability of polymers. Fire retardant solutions delay the flash over because of their low contribution to the fire. On the other hand, fire resistant solutions act after flash-over and it limits the physical

propagation of fire from one area to another. Ignitability and flammability are two main important parameters of fire retardancy of materials [96].

Heat, combustive element and fuel are the main three elements for creating fire. When these three elements come together, combustion occurs [96].

Depending on the intensity of heat source and of the intrinsic characteristics of the polymer, the source of heat increases the temperature of the polymer. Pyrolysis is the decomposition of polymer by high temperature. As the decomposition occurs, organic materials that are volatile and flammability mainly free radicals are formed with low molecular weight [96].

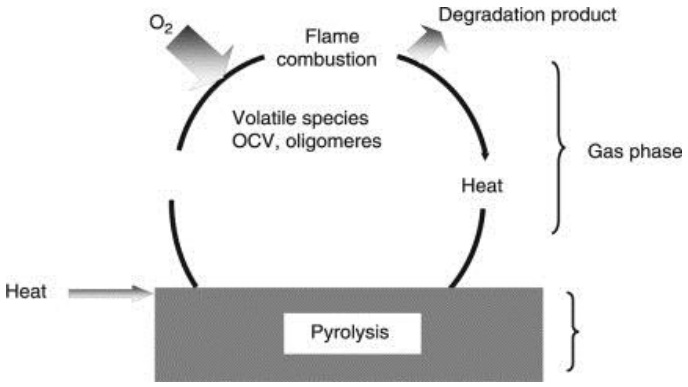


Figure 2.17 : Decomposition of Polymer

For catching fire, a critical level of the flammable volatile species in combination with oxygen must be reached. The flame created becomes the heat source and maintains the decomposition of the polymer. This phase is called as condensed phase [96].

Fire cycle must be broken for prevent fire of polymer. For this aim, heat, fuel or combustion must be suppressed. The cycle has different steps and these steps occur at gas or condensed phase [96].

In the polymer thermal degradation, polymer releases very reactive free radical species such as H• or OH•. These species continues the combustion in the gas phase. If the halogenated flame retardants are added, it can slow down the radical formation. In the burning process, the flame retardant is decomposed and halogenated radical species are created such as Cl•or Br•. They neutralize the radical species and results in the chain decomposition and combustion [96].

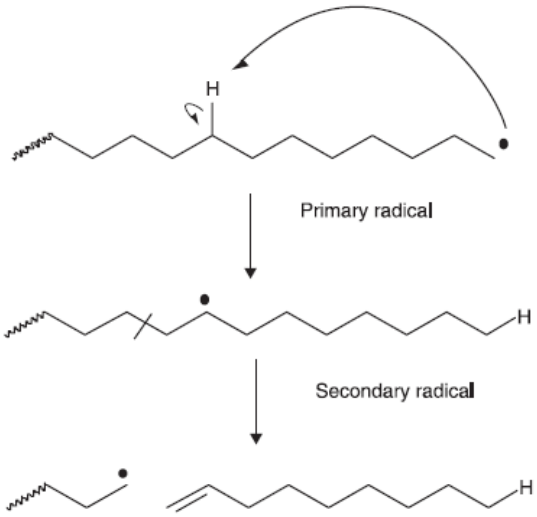


Figure 2.18 : Decomposition: Example of Free Radical Formation [96].

2.11.2. Actions of fire retardants

Fire retardants work physically or chemically. It is known that chemical actions of fire retardants are more effective [97].

2.11.2.1. Physical action

For physical action of fire retardant, hydrated fillers can be used. The fire retardants decompose endothermically and they remove heat from the material and flame. Gases developed dilute the flammable vapors and ignition limits of temperature and mass can not be reached for fire. Carbon nanotubes create physical action as well. They increase thermal conductivity of material and heat is dissipated away from ignition source [97].

An inert material can be utilized to create a barrier between heat source and polymer. For example, carbon black can ne used as an inert material. In addition, decomposition of ATH creates aluminum residue, which can be used for barrier purposes. The barrier protects the pyrolysis zone from oxygen and slows down the rate of fuel production. It also blocks volatile gases to reach the flame and retard heat transfer with the help of creating a radiation shield and thermal insulation. For advanced fire retardancy, a swollen barrier which is called as intumescent fire retardant can be developed. Finally, fillers reduce the content of flammable material and reduce flammability [97].

2.11.2.2. Chemical Action

Some fire retardants decompose and create gases which react in the gas phase. Radical propagation is blocked with this mechanism. The flame is quenched due to the unreactive radical species. These species cannot propagate the free radical reaction of flaming combustion. In a fire retardant type of char development, combustible gases are eliminated. In this type of fire retardants, polymer is dehydrogenated, unsaturation, crosslinking and cyclisation occurs as well. The char needs higher temperature to burn, for that reason the flame is deprived of fuel. At the end, the char act like a physical barrier to heat and fuel transfer [97].

2.11.3. Flame retardant types

2.11.3.1. Condensed phase char formation

Char forming flame retardants are materials that react chemically with a thermally decomposing polymer in order to form new and more stable bonds than bonds broken by the heat. Since the radicals in the condensed phase have more residence time in the condensed phase before volatilizing, they react with themselves rather than pyrolyzing and combusting. These polymers keep the heat release rate slow by binding up polymeric fuel into highly cross-linked graphitic or glassy-carbon char since only a small portion is being pyrolyzed for combustion. This class include phosphorus flame retardands adn intumescent fire-protection packages [98,99].

The charring layer protects the matrix of the material. Its properties depend on physical and chemical structure. There are two typical charring structure of char layers. Firstly, the char layer has integrated closed honeycomb pores. This structure supplies adequate temperature grads in the charring layer and the molten mass and matric below are protected. Secondly, the char layer has a lot of channels and apertures. The gas and molten mass of polymers can overflow to the entry of the flame-region. This structure is non-ideal and the isolation effect of heat transfer is inferior [98,99].

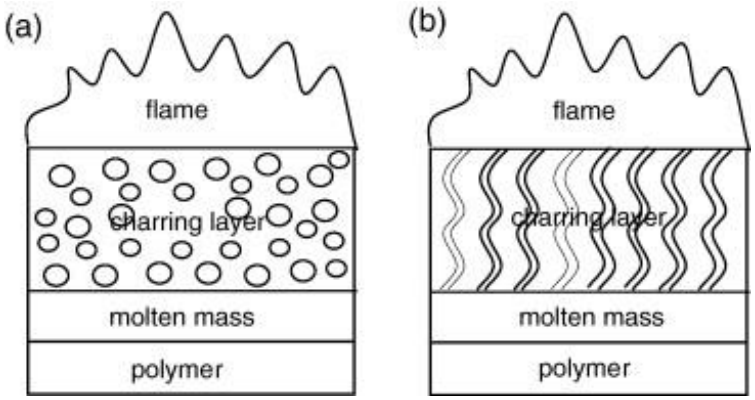


Figure 2.19 :

Figure 2.20 : Structures of Charring Layer: (a) Uniformity and (b) Asymmetry [98].

2.11.3.2. Endothermic cooling

This class of flame retardants decomposes endothermically to cool the condensed phase when heated. This act prevents prevents further heat-induced decomposition and pyrolysis. During decomposition, the flame retardant generally releases a nonflammable gas and dilutes the fuel in the vapor phase. This behaviour further delays or prevents the ignition and allows self-extinguishment when flame is removed. The examples of this type are mineral fillers and organic carbonates [99].

2.11.3.3. Vapor phase radical inhibition

Some flame retardants behave as vapor phase radical inhibitors. They block free-radical propagation reactions on the areas subjected to flame by pyrolyzing with the polymer fuel and fragmenting into stable radicals. Stable intermediates, whose reactions give less heat than the normal free-radical reactions are deliberately formed in order to decrease the heat in the subjected area. Therefore, free-radical cascade reactions will stop after enough radicals and heat is removed. The principle of Halon fire-extinguishing agents is an example of this mechanism [99].

2.11.4. Intumescent

It is a technology that the flammable material foams and creates an insulating barrier in the time of exposure to heat. A thermal and physical barrier is formed to underlying substrate resulting in a block for high temperatures and flame spreading. The heat exposure initiates a chemical process which results in intumesce. This intumesce and porous layer forms the insulation effect. As the temperature of the

material increases in the case of fire, the thermoplastic matrix melts. When the fire retardant material melts, an endothermic gas producing chemical reaction is triggered. The gas is gathered in small bubbles with creating foam [100].

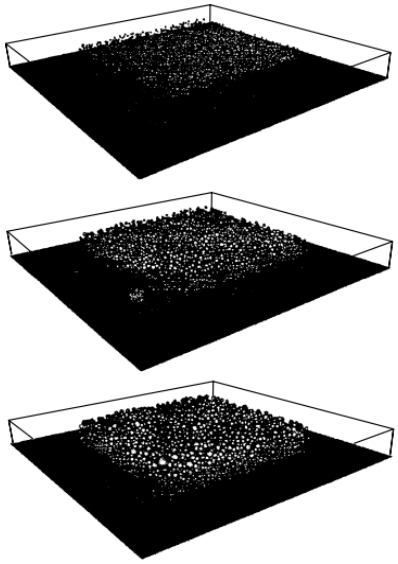


Figure 2.21 : Development of 10 000 Bubbles With Time Upon Exposure To The Heat Flux [100].

2.12. Fire resistance studies on polyurethane foam

PU foams have cellular structure and their density is low. These properties result in PU foam to be highly flammable material. In addition, PU foams burn rapidly. A high rate of heat is released during burning and smoke generation, toxic gases are high as well. Flame retardants can be added to PU foam for this purpose. Generally, halogen compounds, phosphorus compounds, metal hydrates and antimony oxide (Sb2O3) are used in industry. However, despite being effective flame retardants, halogen containing flame retardants have toxic effects and heavy metal oxides (Sb2O3) are harmful for human health and environment. Some bromine-containing (e.g brominated diphenyl oxide flame retardants) are banned due to high toxicity. Therefore a new alternative, which is phosphorus-containing flame retardants, are being investigated. Nitrogen containing flame retardants are eco-friendly and release of toxic gases is slow. Smoke formation is slower as well [95].

In a study on fire resistance of rigid PU foams, melamine and cardanol-derived Mannnich base polyol is synthesized. Cardanol is firstly reacted with paraformaldehyde melamine and diethanolamine in order to obtain mixed Mannich

bases. They are subsequently propoxylated to give the Mannich base polyol. This polyol and polyisocyanate isocyanate is reacted to get rigid PU foam. Expandable graphite ammonium polyphosphate and diethyl ethylphosphate are added to the system for flame retardancy. It is observed that thermal stability of flame retardancy of foam are increased. Expandable graphite is the most effective one. Flame retandant filled rigid PU foam has better compressive strength, thermal stability, char residue, heat release and smoke emission [95].

Sepiolite and montmorillonite can be used for flame retardancy aims. Styrene–butyl acrylate copolymer based fire retardant coatings were prepared with addition of sepiolite and montmorillonite and it is observed that they improved the sustained heat resistance of the fire protecting shield [101].

Montmorillonite creates fire resistance in layer by layer applications of coatings. As an effective alternative, layered double hydroxides can be used instead of montmorillonite. Different formulations of layered double hydroxides found as more successful than montmorillonite such as lower ignition resistance and heat release rate. layered double hydroxides also resulted in greater reduction with less layers and lower mass. With only 2 trilayers of layered double hydroxides, flammability of PU foam is decreased significantly. Above 2 trilayers, flammability reduction is not further change [102].

Polyurethane–polyisocyanurate foams (PU-PIR) with different amounts of flame retardants and a layered silicate nanoclay have improved flame resistance as well. 1,1,1,3,3-pentafluorobutane and 1,1,1,2,3,3,3-heptafluoropropane are environmentally friendly blowing agents that is utilized in synthesis of PU-PIR foam. A small amount of water should be used. These PU-PIR foams showed better fire resistance than classical PU and unmodified PUR–PIR foam. It is also observed that addition of layered silicate nanoclay significantly reduced the flammability when used with flame retardants such as reactive bromine, phosphorus compounds, and zinc stannate [103].

2.13. Characterization Methods

Polymers can be characterized physically by a lot of methods. The methods used in this study are explained below.

2.13.1. Thermal gravimetric analysis

In thermal gravimetric analysis (TGA), a small sample i.e about 10 mg is continuously weighed as the temperature linearly increases. The atmosphere can be air or nitrogen. A graph shows weight loses due to desorption of gases or decomposition. It is especially used for determination of filler quantity in materials. The advantage of TGA is its simple usage [104].

2.13.2. ^{1}H nuclear magnetic resonance

Nuclear magnetic resonance (NMR) is a spectrometric technique to determine chemical structures of materials. The theory behind NMR is the alignment of the nucleus in the direction of applied magnetic field. Energy is required to reverse the alignment, which depends on applies magnetic field and nature of nucleus. The reversal is a resonant process and specific to components. By determining energy level transitions for all of the atom in the molecule, properties of components can be revealed. The most common nuclei that is examined are H and C; therefore, 1H NMR and 13C NMR the most used NMR systems and 1H NMR is more sensitive than 13C NMR . 13H NMR is used for structure determination of organic molecules [105].

2.13.3. Fourier transfer infrared spectrometer

In Fourier Transfer Infrared Spectrometer (FTIR), electromagnetic spectrum goes through the sample. Sample absorbs specific wavelengths and is excited to higher energy level. The molecules have specific frequencies that they absorb the spectra and they vibrate or rotate. There are four kinds of energy types that molecules have: electronic, vibrational, rotational and translational. All vibrations and rotations of molecules are not infrared active. Dipole moment of the molecule must change for FTIR analysis of sample. By using FTIR, presence of chemical groups can be determined. It is also can be used for determination of certain functional groups, structure of polymer, polymer degradation process and to examine polymerization processes [105,106].

2.13.4. X-Ray diffraction

X-Ray Diffraction (XRD) is used for determination of crystallinity, crystal size, orientation of crystallites and phase composition if the material is semi-crytalline.

Phase changes in order to determine lattice strain, crystalline modulus and structure of polymer can be studied as a function of stress or temperature [107].

2.13.5. Limiting oxygen index

Oxygen index methods used to measure the flammability of polymers. Effectiveness of fire-retardants are also investigated by limiting oxygen index test. In this method,

the tendency of a material to sustain a flame is measured. It provides convenient, reproducible numerical measure of flammability. It is generally reported as a percentage, not fraction. Air contains 20.95%oxygen, therefore, a polymer with a limiting oxygen index less than 20.95% burns in the air easily [108].

3. EXPERIMENTAL PART

This part contains information on materials used in the laboratory. The procedure of experiments are described in the detail. Applied characterization methods for the chemical and physical analysis are also denoted.

3.1. Materials

Materials used in ketonic resin synthesis:

- Cyclohexanone
- Formaldehyde (37% solution)
- Anhydrous NaOH pellets
- Cyclohexane
- Sepiolite

Sepiolite is supplied from Sivrihisar, Turkey by Tolsa Group. The chemical analysis is carried out by ICP (Inductively Coupled Plasma Spectrometer) in ACME Analytical Lab, Canada. According to the chemical analysis, sepiolite contains 49.85% SiO2, 2.38% Al_2O_3, 0.87% Fe_2O_3, 20.15% MgO, 2.65% CaO in weight. Sepiolite has 85 ± 3% purity according to mineralogical analysis of the Tolsa Group performed using Shimadzu XRD-6000 equipped with Cu X-ray tube (λ= 1.5405Å) with Dolomite, Calcite, Albite and Quartz.

- Montmorillonite
- Alendronic acid
- Materials used in foam polyurethane synthesis:
- Polyol

Polyol is retrieved from Poliser-Flokser Group.

- Isocyanate:

Isocyanate is retrieved from Poliser-Flokser Group

- Dichloromethane

3.2. Instruments and Analysis

Fourier transform infrared (FTIR) spectra is obtained from an FTS-6000 Excalibur FTIR with an attenuated total reflectance sampling accessory. It uses software of Varian Resolutions. The data are obtained directly from the sample without KBr discs.

^{1}H- NMR spectra is obtained by Agilent VNMRS (Varian 500 MHz) spectrometer at room temperature. $CDCl_3$ is used as deuterated solvent. Chemical shifts (δ in ppm) were reported down field from tetramethylsilane.

TG/DTA spectra is obtained by SII 7200 Exstar, which is ambient to 1100°C.

3.3. Procedure

Whole study can be divided into three steps in sequence. Firstly, cyclohexanone-formaldehyde resin and their clay or alendronic acid modified versions are synthesized. Secondly, polyol is modified with CFR and modified CFR. These polyols are used for foam polyurethane synthesis. Finally, the characterization of resins and analysis of polyurethanes are carried out.

3.3.1. Synthesis of cyclohexanone-formaldehyde resin

The desired molar ratio of ketone/formaldehyde is 1/1.06. By using this ratio, the required volumes of chemicals are calculated. After that, 52 mL of cyclohexanone, 12.5 mL of cyclohexane and 15 mL of 37% formalin are poured in a three necked round-bottom flask. 20 g of andhyrous NaOH pellets are mixed with 100 mL of water and 20% NaOH solution is obtained. NaOH is the catalyst of this reaction. After this, the flask is inserted into a water bath, which is onto the heater. The heater is turned on and begun to increase the temperature of the mixture. The temperature is set to 80°C. The chemicals in the flask are being mixed with a mechanical mixer. A condenser is also connected to the flask for reflux.

As the mixture is mixing and the temperature of mixture rises, a few drops of 20% NaOH solution is added to the flask slowly until the pH value is 11-12. At 80°C, reflux begins and 50 ml of 37% formalin is added dropwise. pH value of the mixture

is controlled and set at 11-12 by adding 20% NaOH when pH lowers until the reaction is complete.

The reaction time is 5 hours. After 5 hours, a yellowish, two layered resin is formed. As the reaction is terminated by shutting off the mixer and heater, the resin is poured down into a beaker and washed with water. The resin in the baker is dried in vacuum oven for 5 hours at 80°C. The dried resin is pulverized by a mortar and pestle. Finally, the weight of the product is measured by a precision weighning scale.

3.3.2. Synthesis of clay modified CFRs

CFR is modified with sepiolite and montmorillonite with different percentages.

3.3.2.1. Synthesis of sepiolite modified CFRs

CFR is modified by addition of sepiolite. It is added to the mixture as 1% wt, 3% wt and 5%wt of cyclohexanone, which is called Sep1-CFR, Sep3-CFR and Sep5-CFR respectively. 0.52 g sepiolite is added for Sep1- CFR. 1.56 g of sepiolite is used for Sep3- CFR. Lastly, 2.6 g of sepiolite is used for Sep5- CFR.

Required amount of sepiolite is put to the three necked round flask with 52 ml of cyclohexanone, 12.5 mL of cyclohexane and 15 mL of 37% formalin at the beginning of reaction. Since clay is added to the mixture, the mixing should be done faster for homogenous resin. pH of the mixture is set to 11-12 by adding 20%NaOH solution slowly. As the reflux begins, 50 mL of 37% formalin is added to the system dropwise. The rest of the procedure is the same with CFRs synthesis procedure such as pH control, reaction time, washing of the resin with water and drying the resin in the vacuum oven.

3.3.2.2. Synthesis of Montmorillonite modified CFRs

CFR is also modified by addition of montmorillonite. It is added to the mixture as 1% and 5% of cyclohexanone and they are called as MM1-CFR and MM5-CFR respectively. 0.52 g montmorillonite is added for MM1-CFR and 2.6 g of montmorillonite is used for MM5- CFR.

52 ml of cyclohexanone, 12.5 ml of cyclohexane and 15 ml of 37% formalin mixed with montmorillonite at the beginning of reaction. The mixing should be more vigorously since the clay is added to the mixture. pH of the mixture is set to 11-12 by adding 20% NaOH solution dropwise. As temperature raises up to 80°C, reflux begins and 50 ml of 37% formalin is added to the system slowly. The rest of the procedure is the same with CFRs synthesis procedure such as pH control, reaction time, washing of the resin with water and drying the resin in the vacuum oven.

3.3.3. Synthesis of alendronic acid modified CFRs

Not only clay but also alendronic acid is used for modification of CFR. Alendronic acid is added to the system as 5%, 10% and 20% of cyclohexanone. These modified resins are called as AA5-CFR, AA10-CFR and AA20-CFR. 2.6 g alendronic acid is added for AA5-CFR. 5.2 g of alendronic acid is used for AA10-CFR and 10.4 g alendronic acid is added for AA20-CFR.

Like synthesis of other resins, 52 ml of cyclohexanone, 12.5 ml of cyclohexane and 15 ml of 37% formalin mixed with the modifier i.e alendronic acid at the beginning of reaction. pH of the mixture is set to 11-12 by adding 20% NaOH solution dropwise. Since the modifier is an acid, more NaOH is added in order to increase pH up to 11-12. Slowly, temperature rises up to 80°C and reflux begins. At this stage, 50 ml of 37% formalin is added to the system slowly. The rest of the procedure is the same with CFRs synthesis procedure such as pH control, reaction time, washing of the resin with water and drying the resin in the vacuum oven.

3.3.4. Synthesis of alendronic acid and Sepiolite modified CFRs

These resins are synthesized by adding both alendronic acid and sepiolite to the CFR reagents. Two different resins are sythesized: CFR with 7.5% sepiolite mixed with 10% alendronic acid (Sep7.5-AA10-CFR) and CFR with 20% sepiolite mixed with 10% alendronic acid (Sep20-AA10-CFR). The percentages are calculated in the basis of cyclohexanone weight. Firstly, 3.9 g of sepiolite is mixed with 5.2 g of alendronic acid for Sep7.5-AA10-CFR. Secondly, 10.4 g of sepiolite and 5.2 g of alendronic acid are mixed for the Sep20-AA10-CFR

Sepiolite and alendronic acid are put into the three necked round flask with 52 ml of cyclohexanone, 12.5 ml of cyclohexane and 15 ml of 37% formalin. pH of the mixture is set to 11-12 by adding 20% NaOH solution dropwise. As temperature raises up to 80°C, reflux begins and 50 ml of 37% formalin is added to the system slowly. The rest of the procedure is the same with CFRs synthesis procedure such as pH control, reaction time, washing of the resin with water and drying the resin in the vacuum oven.

3.3.5. Synthesis of alendronic acid and montmorillonite modified CFRs

Montmorillonite and alendronic acid are used as another modifier for CFR. Two resins are synthesized: One with 5% montmorillonite and 5% alendronic acid and one with 10% montmorillonite and 10% alendronic acid. The percentages are calculated in the basis of cyclohexanone weight. Firstly, 2.6 g of montmorillonite is mixed with 2.6 g of alendronic acid for 5% montmorillonite and 5% alendronic acid modified CFR (MM5-AA5-CFR). Secondly, 5.2 g of montmorillonite and 5.2 g of alendronic acid are mixed for the 10% montmorillonite and 10% alendronic acid modified CFR (MM10-AA10-CFR).

Montmorillonite and alendronic acid are put into the three necked round flask with 52 ml of cyclohexanone, 12.5 ml of cyclohexane and 15 ml of 37% formalin. pH of the mixture is set to 11-12 by adding 20% NaOH solution dropwise. As temperature raises up to 80 C, reflux begins and 50 ml of 37% formalin is added to the system slowly. The rest of the procedure is the same with CFRs synthesis procedure such as pH control, reaction time, washing of the resin with water and drying the resin in the vacuum oven.

Table 3.1 : Content of Resin Samples.

Samples	Sepiolite wt%	Montmorillonite wt%	Alendronic Acid wt%
CFR	-	-	-
Sep1-CFR	1	-	-
Sep3-CFR	3	-	-
Sep5-CFR	5	-	-
AA5-CFR	-	-	5
AA10-CFR	-	-	10
AA20-CFR	-	-	20
MM1-CFR	-	1	-
MM5-CFR	-	5	-
MM5-AA5-CFR	-	5	5
MM10-AA10-CF	-	10	10
Sep7.5-AA10-CF	7,5	-	10
Sep20-AA10-CFI	20	-	10

3.4. Synthesis of Foam Polyurethane with Modified Polyol

Produced resins are pulverized. These pulverized resins are dissolved in 4 ml of dichloromethane. The resin is mixed with polyol.

15 g of polyol is poured into a paper cup. 60% of polyol is calculated as 9 g. Therefore, 9 g of modified CFR is stirred for 2-3 minutes by using a mechanical stirrer. After the mixture is homogenously mixed, 18 g of isocyanate is added to the mixture and mixing continued for 10 more seconds. At the end of this process, the product begins to blow. 2 minutes later, blowing is completed and polyurethane hardened. Synthesis of polyurethane foam is completed.

Six foam polyurethane are produced by adding 60% modified CFR to polyol.

Table 3.2 : Added Resins To The Foam Polyurethane.

Added Resin
CFR
AA10-CFR
AA20-CFR
Sep5-CFR
MM5-AA5-CFR
Sep7.5-AA10-CFR

4. RESULTS AND DISCUSSIONS

4.1. Formation Mechanism of Alendronic Acid Modified CFR

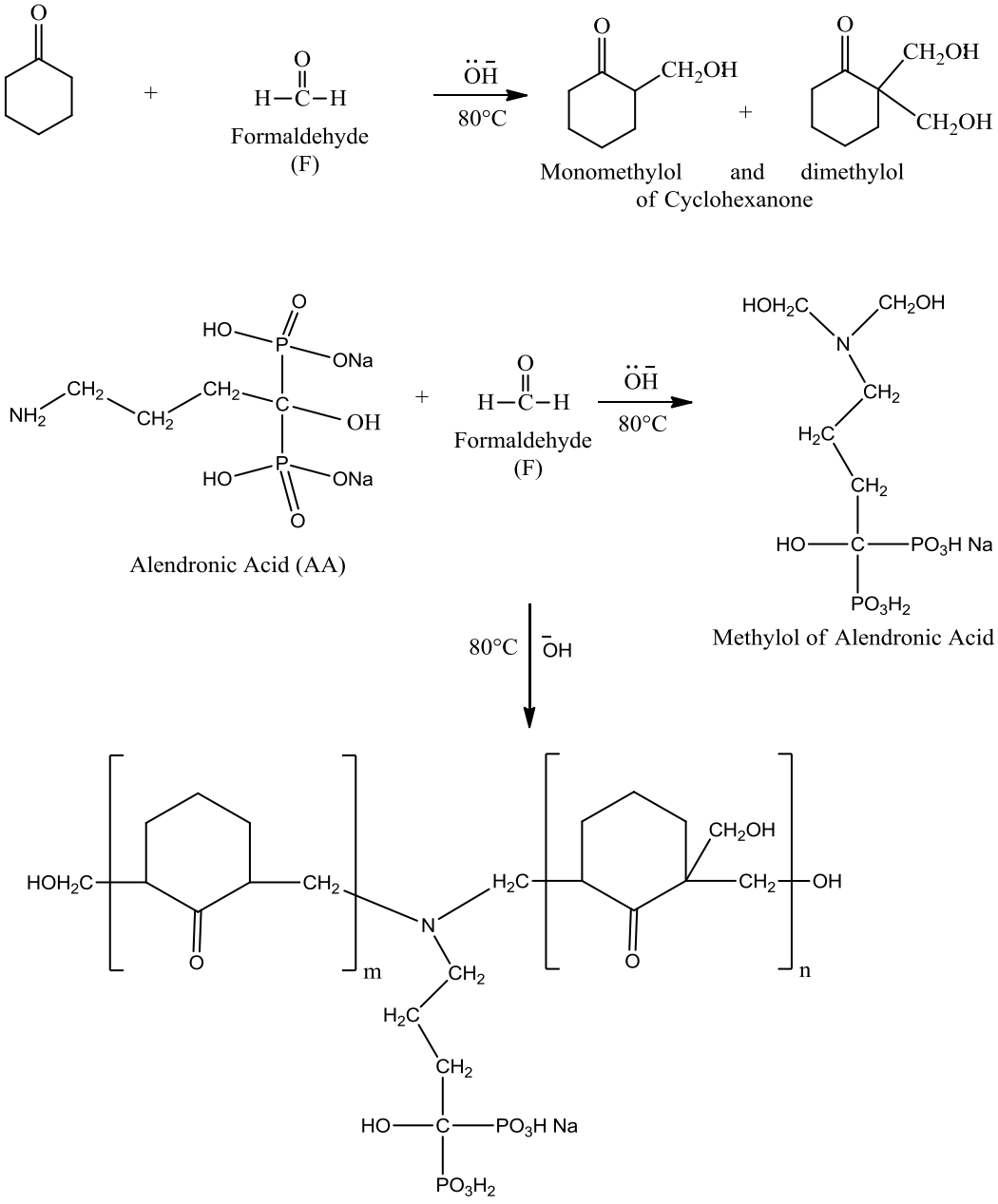


Figure 4.1 : Possible Formation Mechanism of AA-CFR

Both cyclohexanone and alendronic acid probably react with formaldehyde at the beginning of polymerization in the presence of NaOH solution. They form their methylol derivatives such as monomethylols and dimethylols. Condensation reaction between cyclohexanone, alendronic acid, monomethylols and dimethylols present in the reaction media results modified cyclohexanone-formaldehyde resin [37].

4.2. FT-IR Characterizations of Modified Resins

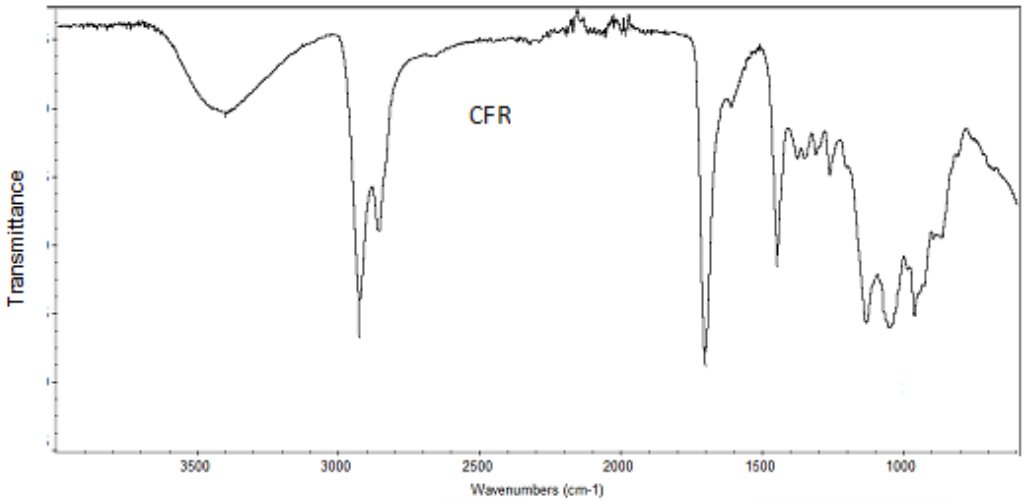
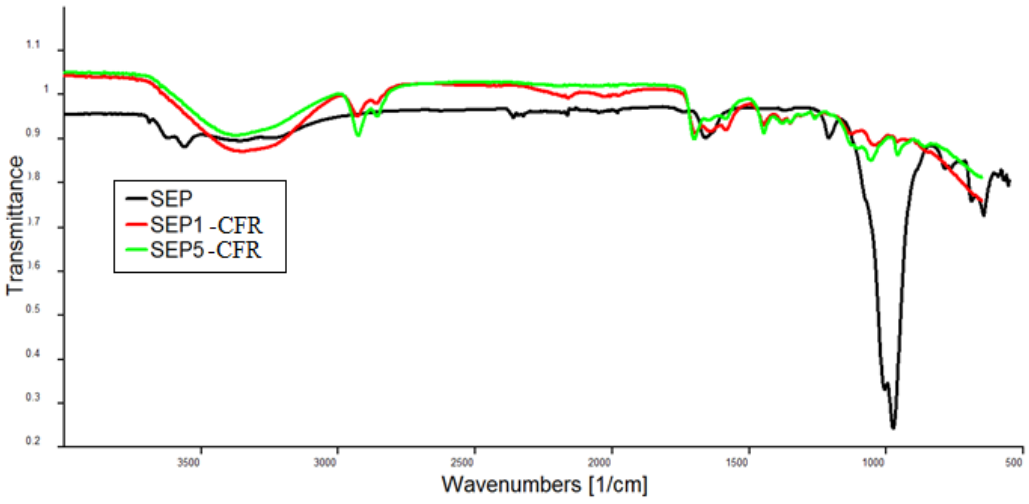


Figure 4.2 : FT-IR of CFR

CFR contains C=O bonds. The stretching peaks of C=O bond of CFR is obtained at 1700 cm^{-1}. C-H bonds show peaks at 2950 cm^{-1}. O-H bond peaks are obtained at 3500 cm^{-1}.



0o

Figure 4.3 : FT-IR of Sepiolite, Sep1-CFR, Sep5-CFR

Higher peak intensities of nanocomposites containing sepiolite (Sep-CFRs) are obtained from ATR-FTIR at about 3500 cm^{-1} and 1630 cm^{-1} due to bound H_2O and about 1000 cm^{-1} due to sepiolite Si-O-Si bond stretching.

While sepiolite has sharp Si-O bond at 1000 cm^{-1}, the peaks of sepiolite modified CFRs at 1000 $cm^{-1}$are smaller. It is concluded that sepiolite is chemically bonded to CFR in Sep-CFRs.

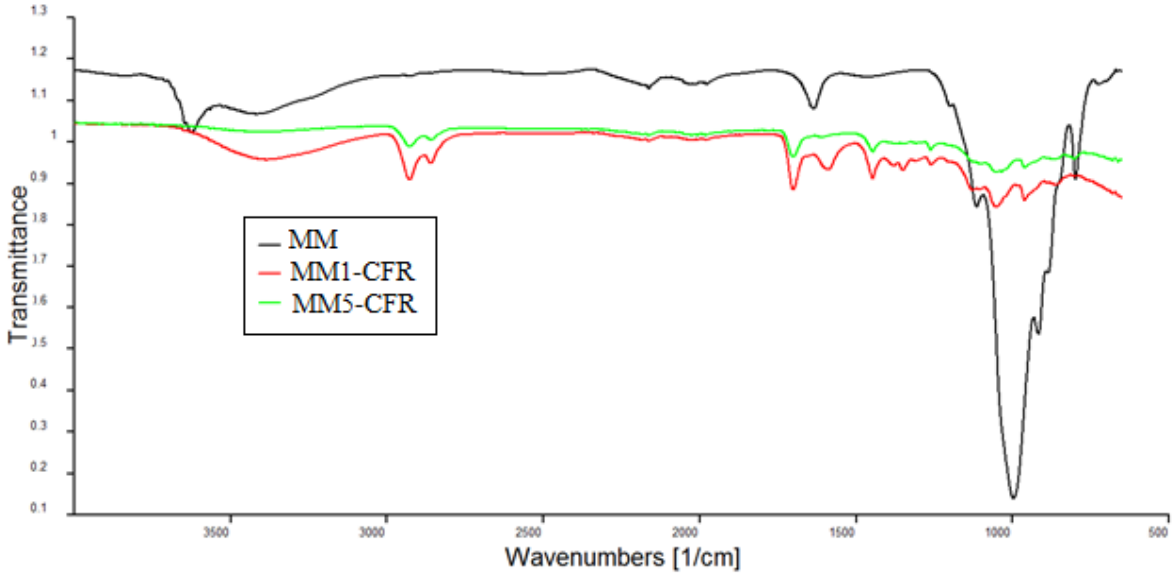


Figure 4.4 : FT-IR of Montmorillonite, MM1-CFR, MM5-CFR

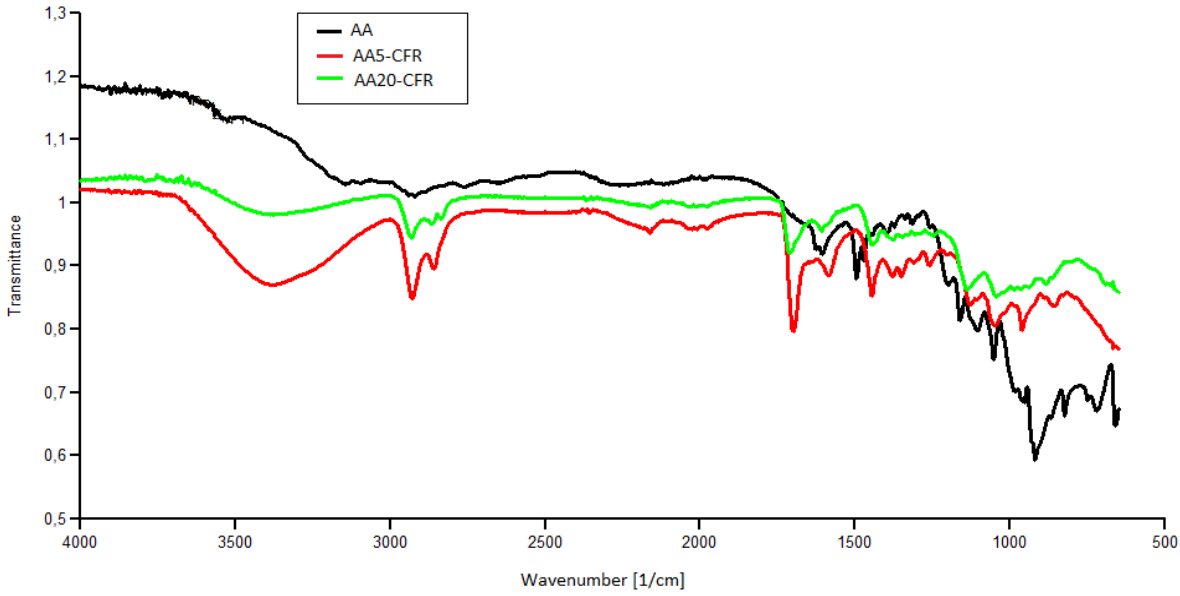


Figure 4.5 : FT-IR of Alendronic acid, AA5-CFR, AA20-CFR

Alendronic acid modified CFRs have peaks at about 2700cm^{-1} and 900cm^{-1} due to P-OH of phosphonic acid groups as well as peaks due to CFR. Up to 1000 cm^{-1}, bending peaks of C-C,C-O and C-N are obtained.

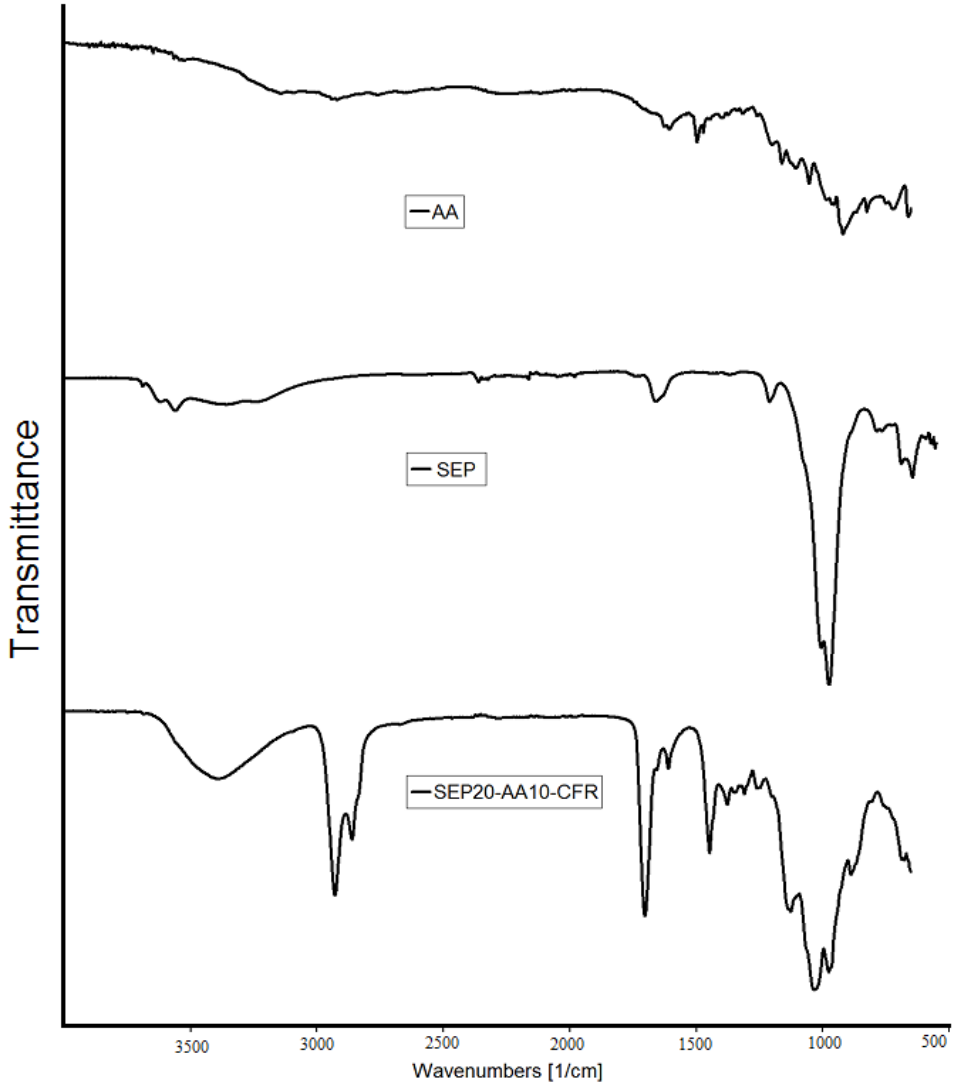


Figure 4.6 : FT-IR of Alendronic Acid, Sepiolite and Sep20-AA10-CFR

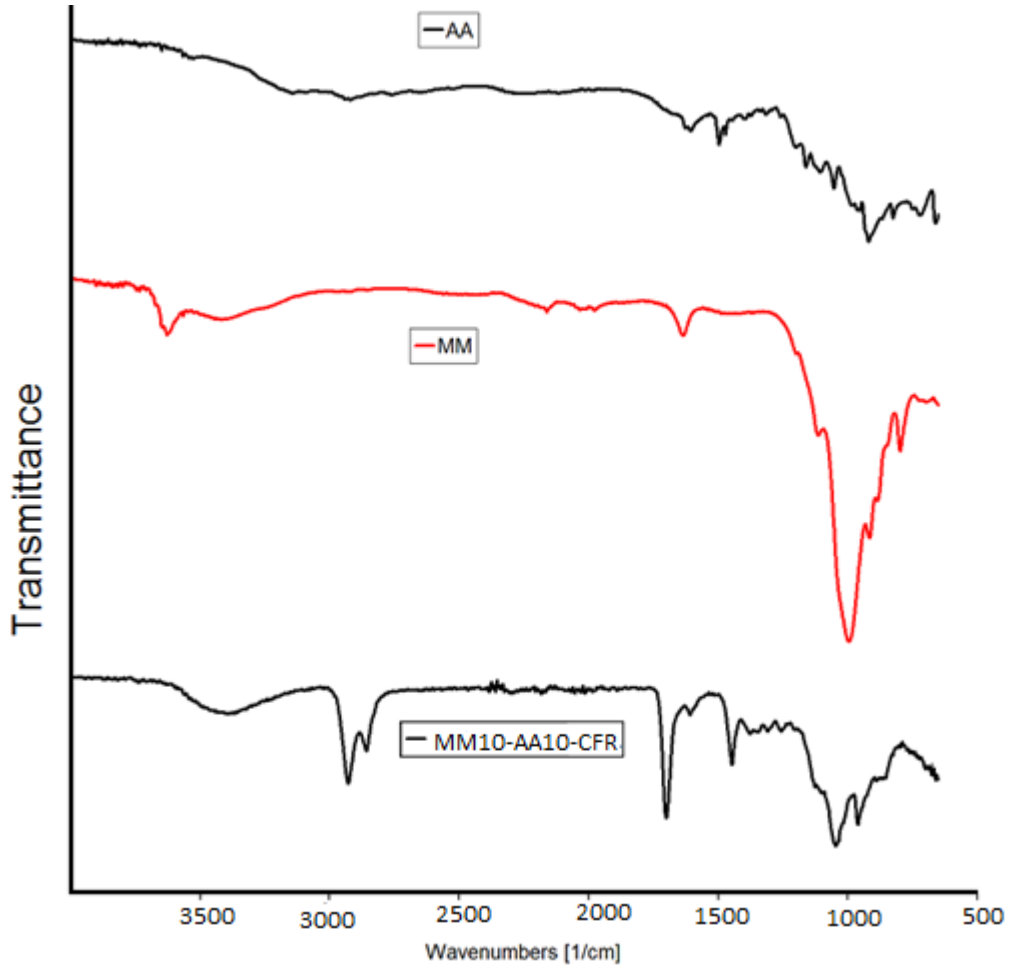


Figure 4.7 : FT-IR of Alendronic Acid, Montmorillonite and MM10-AA10-CFR

As expected MM10-AA10-CFR showed peaks due to P-OH at 2700 cm^{-1}-900 cm^{-1} and adsorbed water and Si-O-Si bonds.

4.3. ^{1}H NMR of CFR

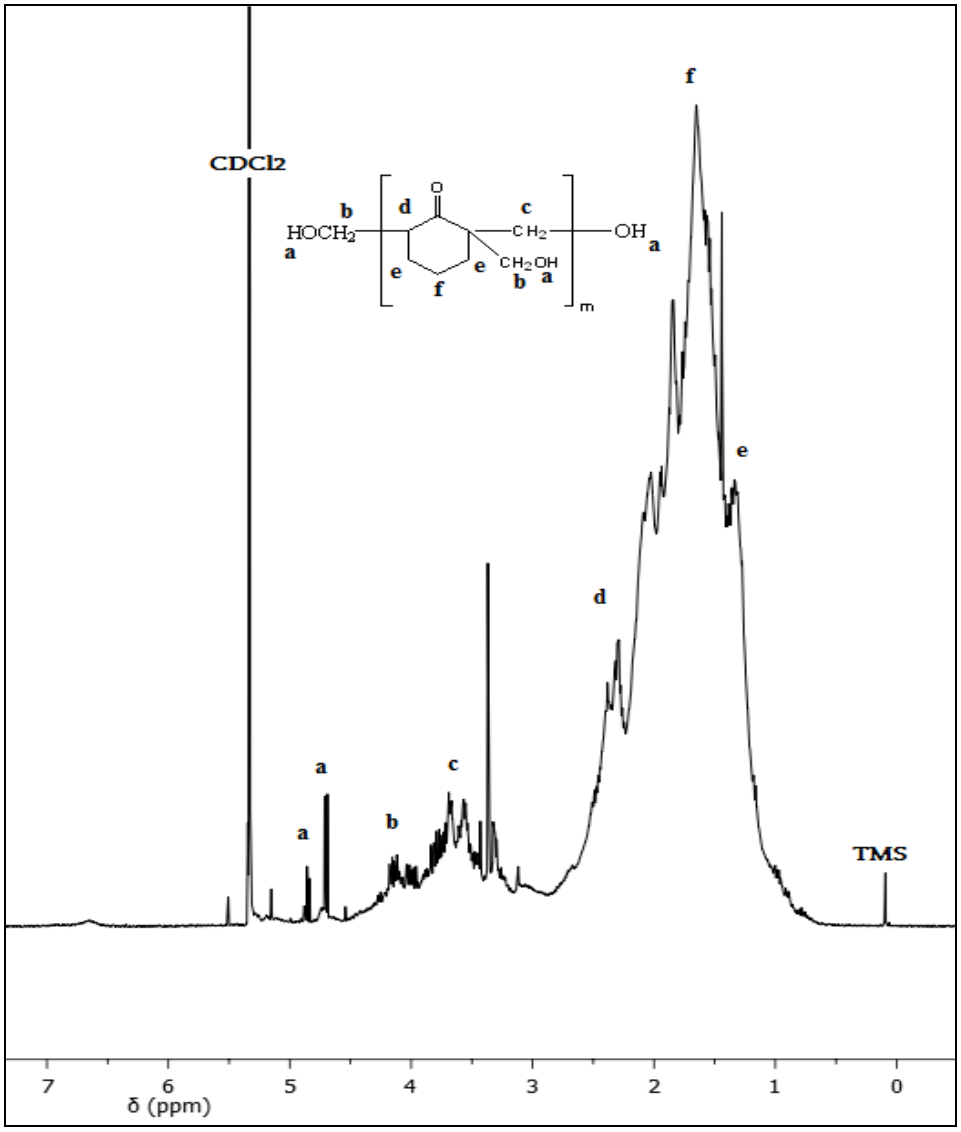


Figure 4.8 : ^{1}H-NMR of CFR

The peaks at 1.1-2.4 ppm shows aliphatic -CH_2 and –CH groups, the peaks at 3.2 – 4.2 shows–CH_2 methylen bridges and methyl groups and the peaks at 4.5 – 4.8 ppm shows–OH groups of the methyl groups .

4.4. Solubility of Alendronic Acid and Clay Modified CFRs

Table 4.1 : Color and Solubility of Alendronic Acid and Clay Modified CFRs.

Samples	THF	DMSO	$CHCl_3$	CH_3OH	DMF	$(CH_3)_2CO$	DCM	EMK
CFR	s	s	s	sl	s	sl	s	s
AA5-CFR	sl	ins	ins	ins	sl	ins	s	ins
AA10-CFR	s	s	s	ins	s	sl	s	s
AA20-CFR	s	sl	s	ins	s	ins	s	s
Sep1-CFR	ins	s	sl	hs	s	s	s	s
Sep3-CFR	sl	hs	sl	ins	s	hs	s	s
Sep5-CFR	sl	ins	hs	ins	s	hs	s	s
MM1-CFR	sl	hs	s	s	s	sl	s	s
MM5-CFR	ins	ins	hs	sl	sl	sl	s	s
MM5-AA5-CFR	ins	ins	s	ins	ins	ins	s	ins
MM10-AA10-CFR	s	s	s	hs	s	s	s	-
Sep7.5-AA10-CFR	ins	ins	ins	ins	sl	ins	hs	-
Sep20-AA10-CFR	ins	ins	ins	ins	Sl	ins	ins	-

It is clear that dichloromethane is the most efficient solvent for all type of modified CFR.

4.5. Melting Points of Alendronic Acid and Clay Modified CFRs

Table 4.2 : Melting Points of Alendronic Acid and Clay Modified CFRs.

Samples	Melting Point (°C)
CFR	110
AA5-CFR	107
AA10-CFR	110
AA20-CFR	120
Sep1-CFR	97
Sep3-CFR	125
Sep5-CFR	150
MM1-CFR	114
MM5-CFR	120

From the melting point determination test, it is concluded that as the alendronic acid percentage in CFR increases, melting point of AA-CFR increases as well. In addition, sepiolite and montmorilonite increase melting point of clay modified CFR efficiently.

4.6. TGA Results of Alendronic Acid and Clay Modified CFRs

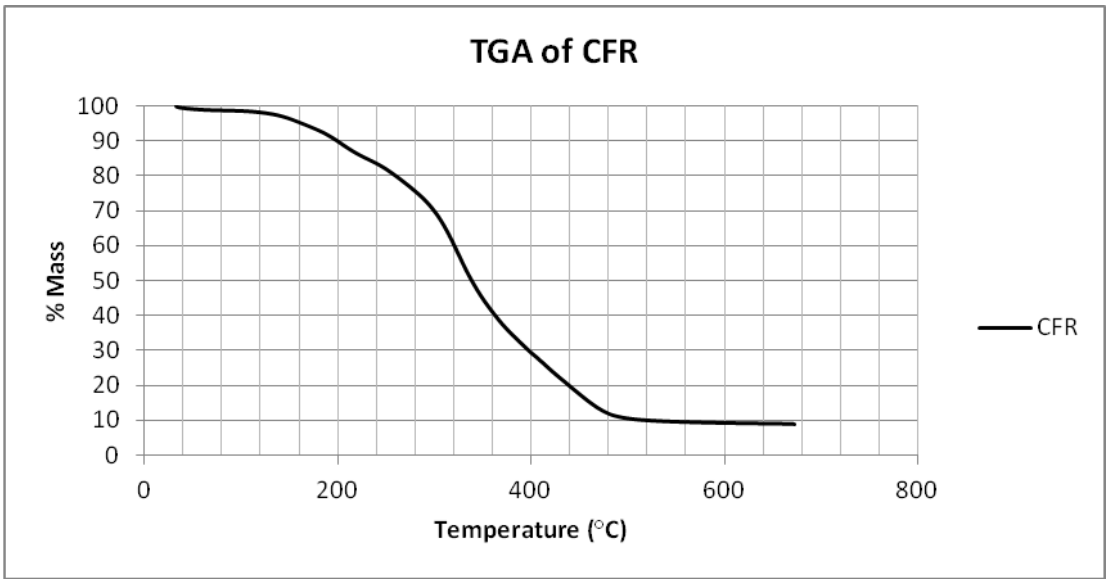


Figure 4.9 : TGA of CFR

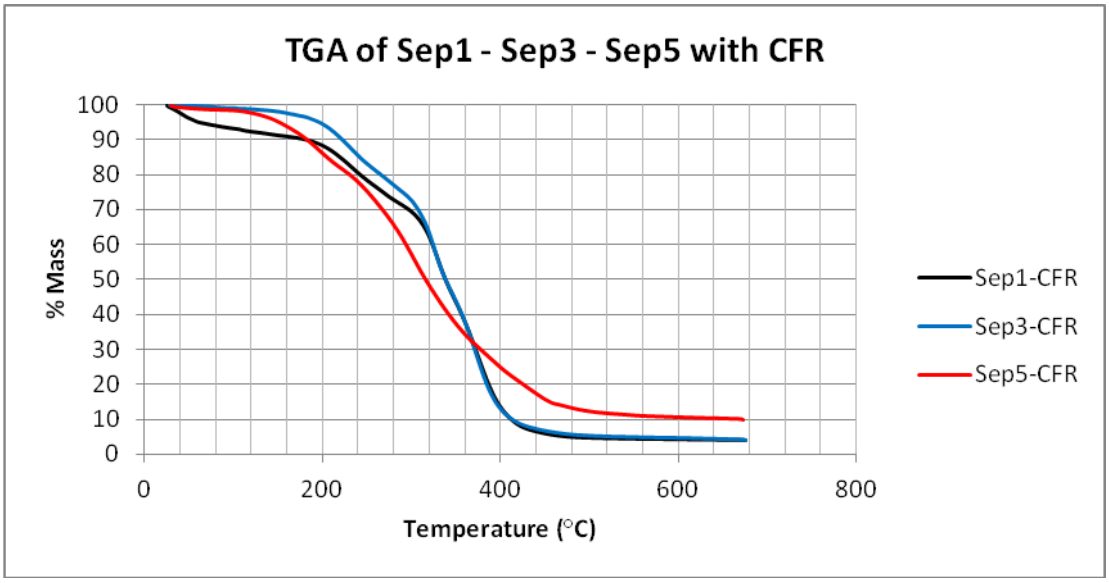


Figure 4.10 : TGA of Sep1-CFR, Sep3-CFR and Sep5-CFR

Since sepiolite has water in its structure, mass of the sample would decrease due to loss of water of sepiolite. Therefore, initial mass decrease does not result from polymer degradation, but water loss. Degradation starts at about 200°C.

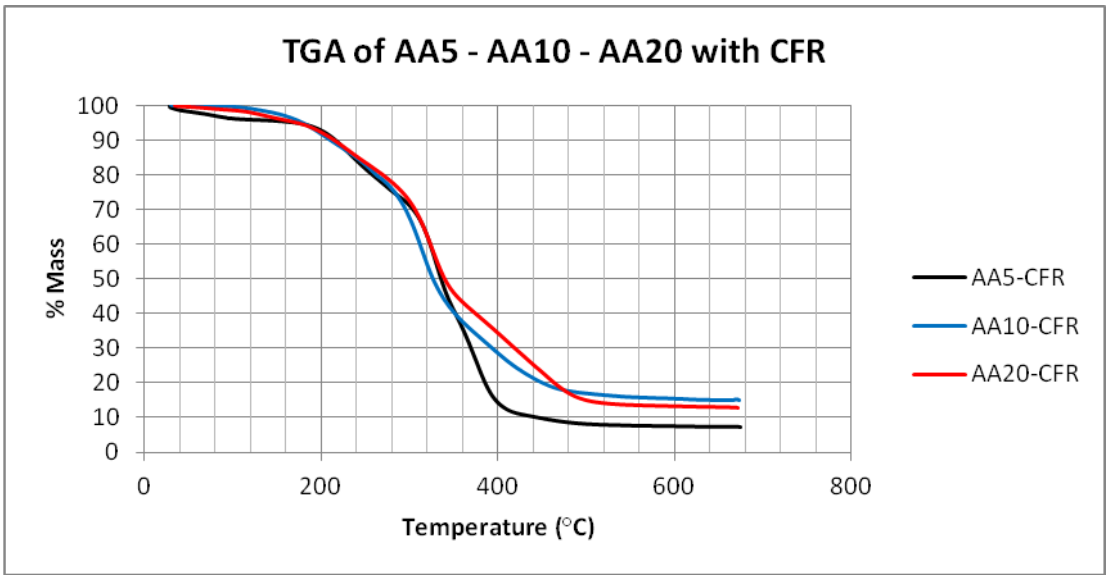


Figure 4.11 : TGA of AA5-CFR, AA10-CFR and AA20-CFR

Polymer degradation does not start immediately as the temperature rises. The mass of polymer decreases due to water loss of montmorillonite. However, at about 200°C, degradation of polymer starts.

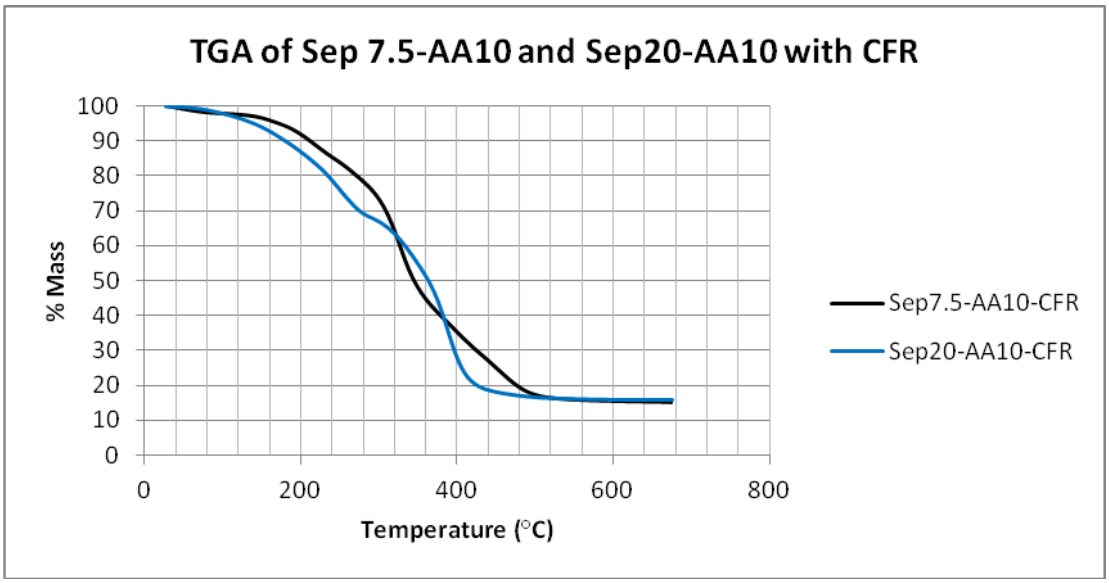


Figure 4.12 : TGA of Sep7.5-AA10-CFR, Sep20-AA10-CFR

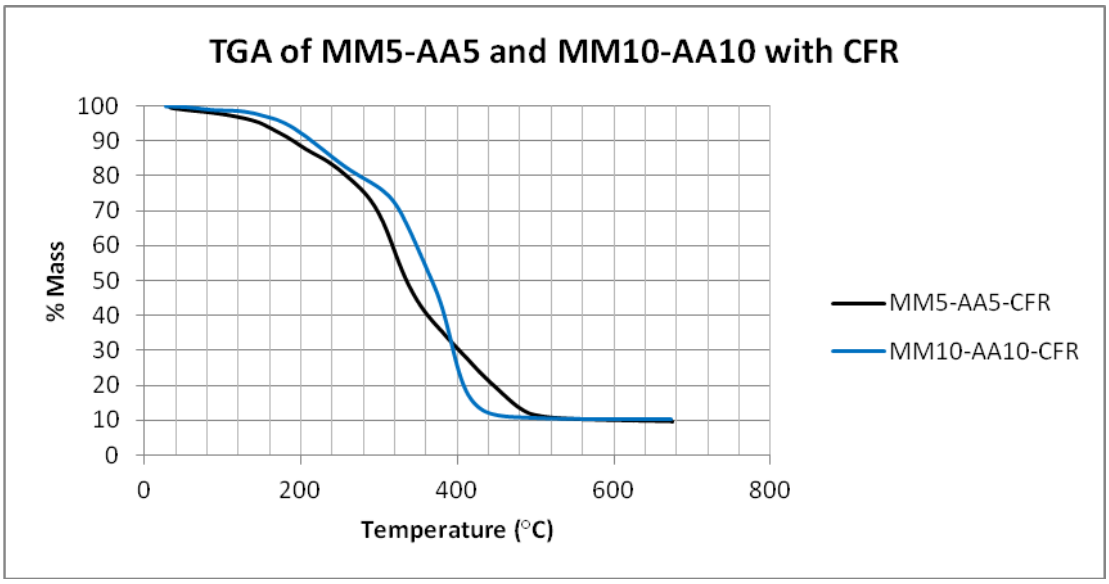


Figure 4.13 : TGA of MM5-AA5-CFR and MM10-AA10-CFR

Table 4.3 : TGA Results of Alendronic Acid and Clay Modified CFRs.

Samples	$T_{\%50}$ (˚C)[b]	Residue (%) at 700(°C)[b]
CFR	338	8.9
AA5-CFR	340	8.0
AA10-CFR	326	15.0
AA20-CFR	340	12.8
Sep1-CFR	339	4.1
Sep3-CFR	338	4.0
Sep5-CFR	316	9.9
MM1-CFR	350	4.6
MM5-CFR	337	5.4
MM5-AA5-CFR	335	9.4
MM10-AA10-CFR	367	10.1
Sep7.5-AA10-CFR	345	15.0
Sep20-AA10-CFR	363	16.0

From TGA results, it is concluded that as the percentage of sepiolite and montmorillonite in CFR increases, fire resistance of nanocomposite increases since the residue at 700 ^{o}C increases. The most efficient one for flame retardancy in all modified resins is Sep20-AA10-CFR as TGA shows.

4.7. XRD Results of Alendronic Acid and Clay Modified CFRs

Since montmorillonite is a layered clay, the resin is filled the layers and it resulted in increase in distance of layers as the montmorillonite content is increased. The layer distance of montmorillonite is 10 Å, however, MM5-AA5-CFR and MM10-AA10-CFR have 15.07 and 16.11 Å respectively as Figure 4.14 represents. Therefore, it is concluded that these nanocomposites have intercalated structures and as the percentage of montmorillonite increases, intercalation of nanocomposite increases as well.

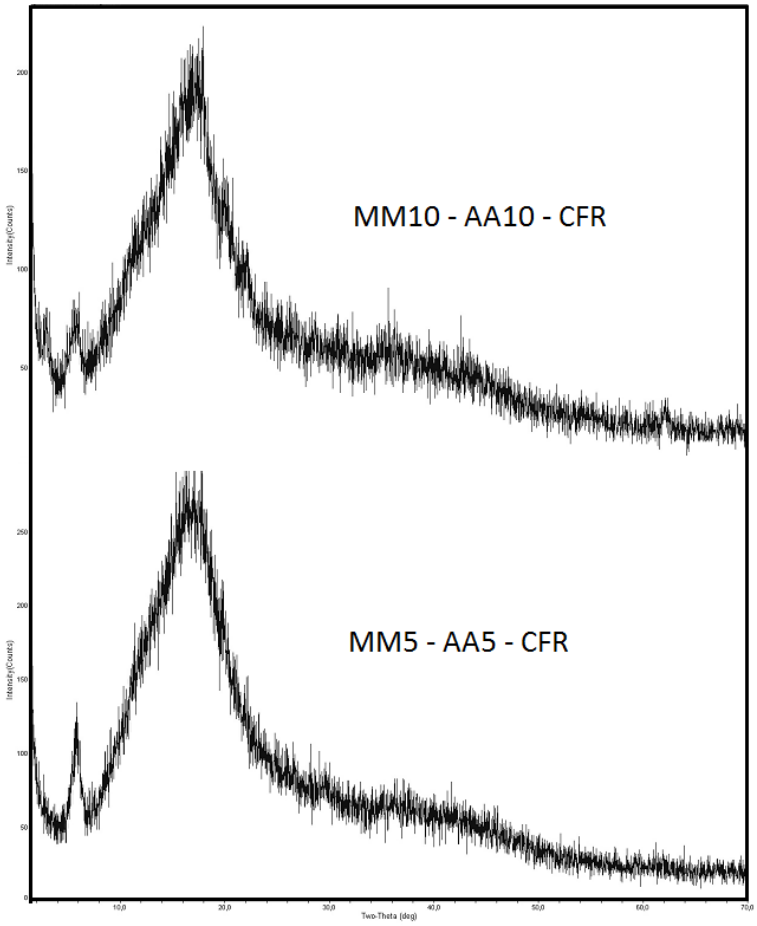


Figure 4.14 : XRD Graph of MM5-AA5-CFR and MM10-AA10-CFR

Distance of sepiolite layers are 11.84 Å. As the Figure 15 and Figure 16 represent, sepiolite is totally dispersed through the matrix, layers are separated from each other and the nanocomposites of Sep1-CFR, Sep3-CFR, Sep5-CFR have exfoliated structures.

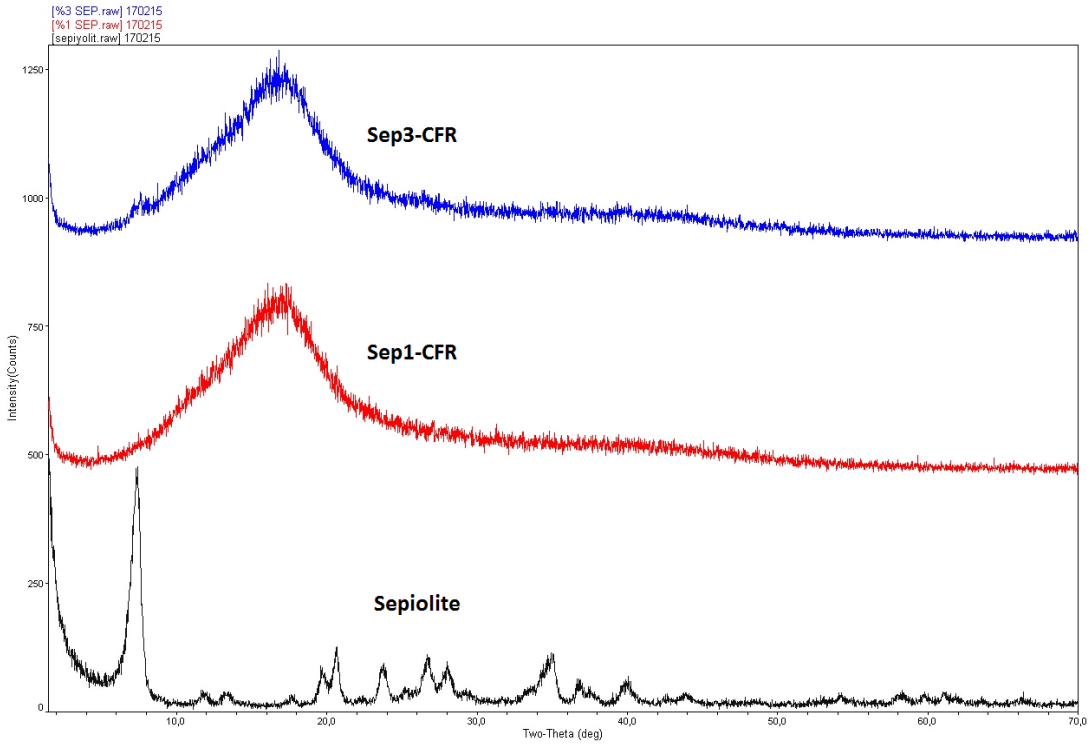


Figure 4.15 : XRD Graph of Sepiolite, Sep1-CFR, Sep3-CFR

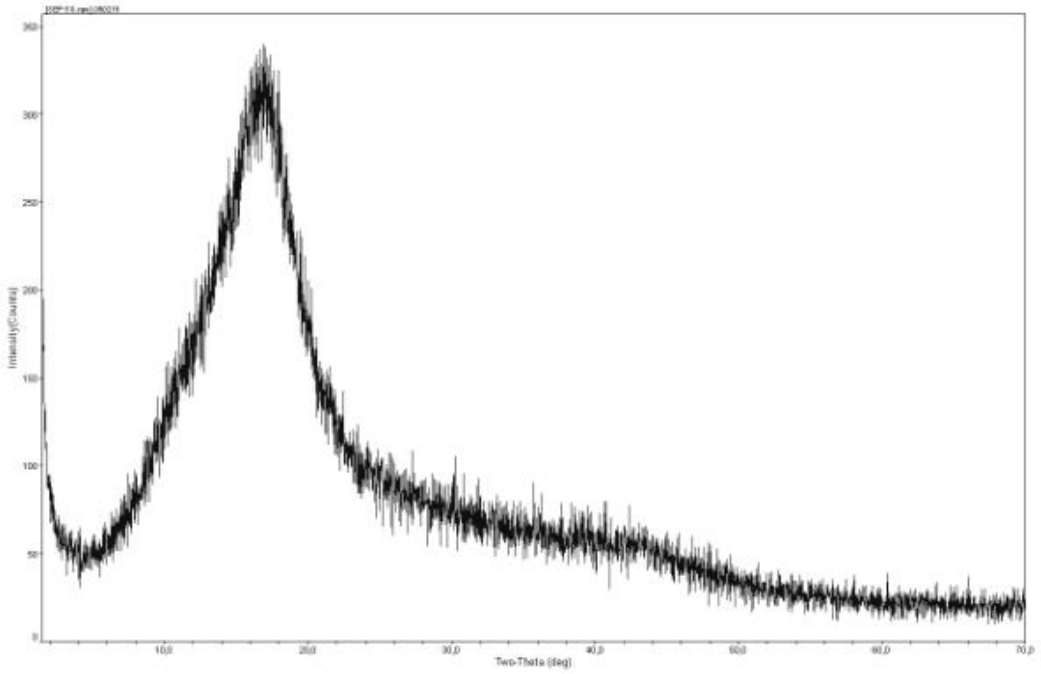


Figure 4.16 : XRD Graph of Sep5-CFR

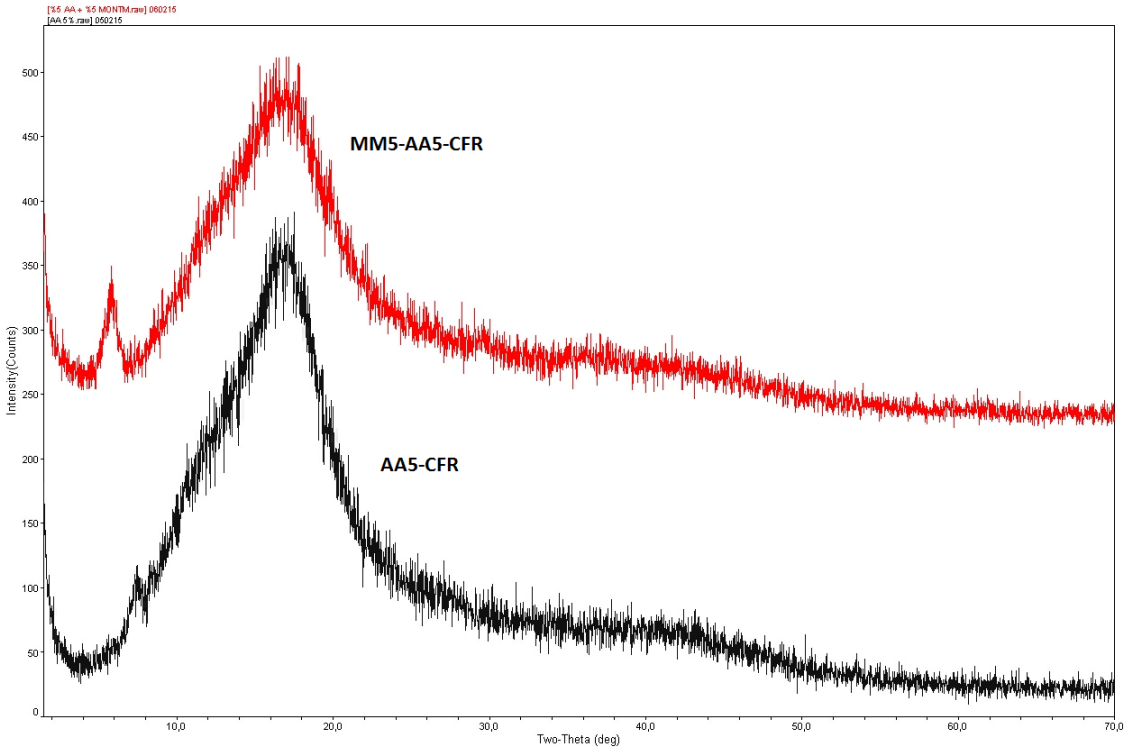


Figure 4.17 : XRD Graph of AA5-CFR and MM5-AA5-CFR

In Figure 4.18, XRD graphs of AA5-CFR and AA10-CFR are represented. Since alendronic acid is an organic substance and not a clay, the layer distances do not change as the alendronic acid content is increased.

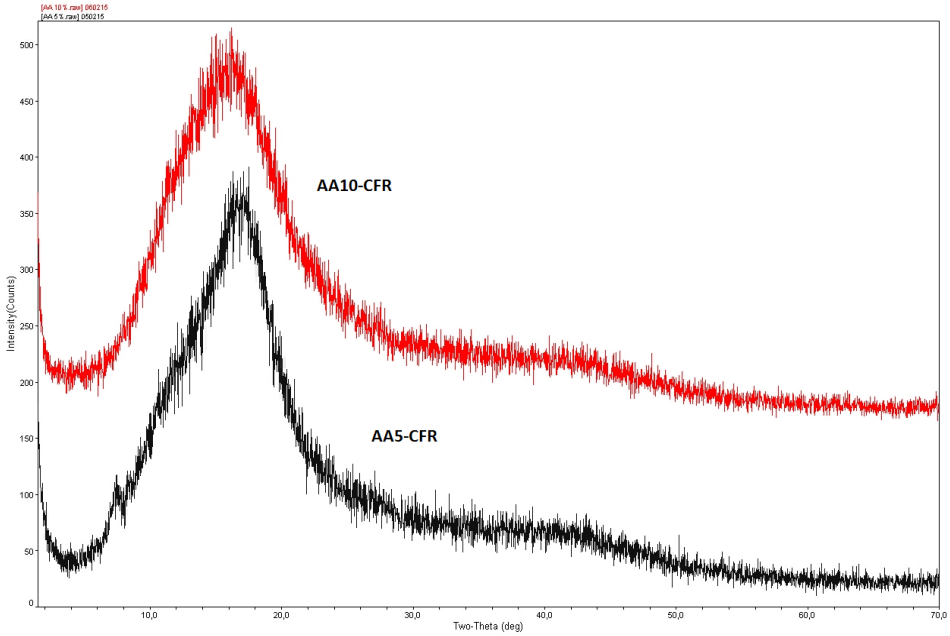


Figure 4.18 : XRD Graph of AA5-CFR and AA10-CFR

In Figure 4.19, At the point 2θ=7.46, sepiolite peaks are observed. These peaks show that nanocomposite is intercalated but not exfoliated.

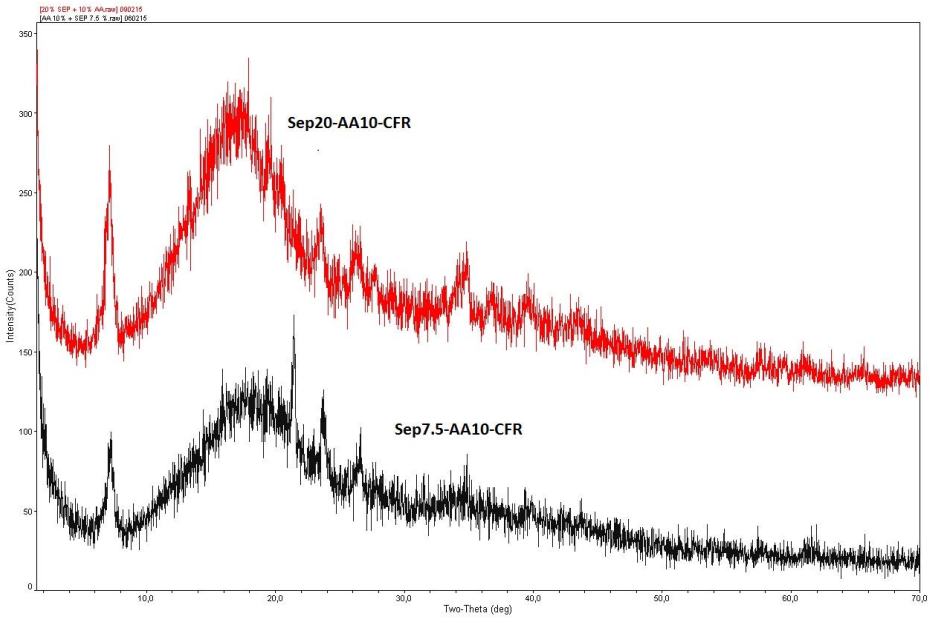


Figure 4.19 : XRD Graph of Sep7.5-AA10-CFR and Sep20-AA10-CFR

Bragg's Law:

$n.\lambda=2.d.\sin\theta$

$\lambda=1.5406$ Å

$n=1$

$d= n.\lambda/2.\sin\theta$

Bragg equation is used in order to calculate distance between layers.

Table 4.4 : XRD Results of Alendronic Acid and Clay Modified CFRs.

Samples	**2θ (deg)**	**θ (deg)**	**d_{001}(Å)**
Sep	7.46	3.73	11.84
Sep1-CFR	16.14	8.07	-
Sep3-CFR	16.84	8.42	-
Sep5-CFR	16.54	8.27	-
AA5-CFR	16.92	8.46	-
AA10-CFR	14.98	7.49	-
Sep7.5-AA10-CFR	7.26	3.63	12.16
Sep20-AA10-CFR	7.18	3.59	12.30
MM5-AA5-CFR	5.86	2.93	15.07
MM10-AA10-CFR	5.48	2.74	16.11

4.8. LOI Analysis of PU Foam

LOI test shows that AA10-CFR, Sep5-CFR and MM5-AA5-CFR has higher LOI than CFR. Therefore, PU with AA10-CFR,, Sep5-CFR and PU with MM5-AA5-CFR are more resistant to fire. At the end, it is concluded that sepiolite, montmorillonite and alendronic acid enhanced the fire resistance of rigid foam polyurethane.

Table 4.5: LOI Results of Nanocomposite and AA Modified PU Foams.

Samples	LOI (%)
CFR	20.4
AA10-CFR	20.7-20.8
AA20-CFR	18.0-18.5
Sep5-CFR	20.6
MM5-AA5-CFR	20.7-21.0
Sep7.5-AA10-CFR	20.0

4.9. Physical Appearances of Alendronic Acid and Clay Modified CFRs

CFR is a yellowish resin.

Figure 4.20 : Physical Appearance of CFR

Sepiolite modified CFR becomes light yellow as the sepiolite percentage decreases.

Figure 4.21 : Physical Appearance of Sep1-CFR, Sep3-CFR, Sep5-CFR

Montmorillonite modified CFR has faint yellow color. It is observed that nanocomposite of MM-CFR is stronger than CFR.

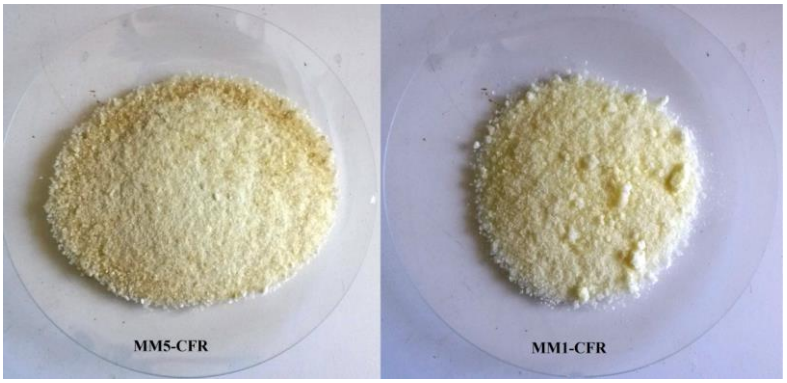


Figure 4.22 : Physical Appearance of MM5-CFR and MM1-CFR

Alendronic acid gives strong yellowish color to the resin. As the percentage of alendronic acid increases, the resin becomes dark yellow and more brittle. It is also observed that the yield of AA20-CFR is lower than other alendronic acid modified CFRs.

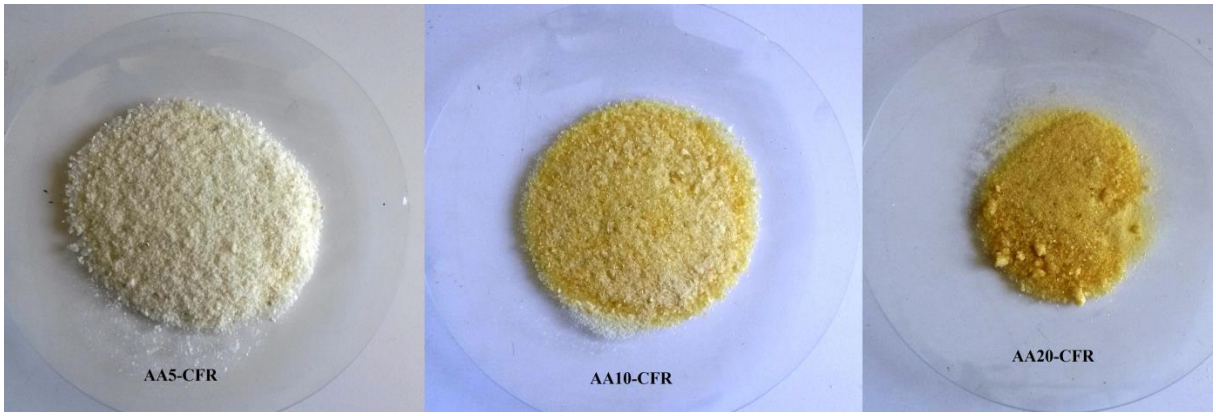


Figure 4.23 : Physical Appearance of AA5-CFR, AA10-CFR, AA20-CFR

In the modification of CFR with montmorillonite, it is observed that it is hard to make a proper nanocomposite of MM-CFR more than 5% montmorillonite since montmorillonite cannot be dispersed in the matrix. However, as the alendronic acid is introduced to the matrix, dispersion of montmorillonite in the CFR is higher. Therefore, it is concluded that alendronic acid act as a compatibilizer in the MM-AA-CFR nanocomposite.

Figure 4.24 : Physical Appearance of MM5-AA5-CFR, MM10-AA10-CFR

Sepiolite can be dispersed in the CFR matrix easier than montmorillonite. The highest percentage of sepiolite in all nanocomposites is 20%, which is a high percentage. It is observed that CFR disperse sepiolite effectively. However, more than 20% sepiolite is not likely since the resin is saturated with clay.

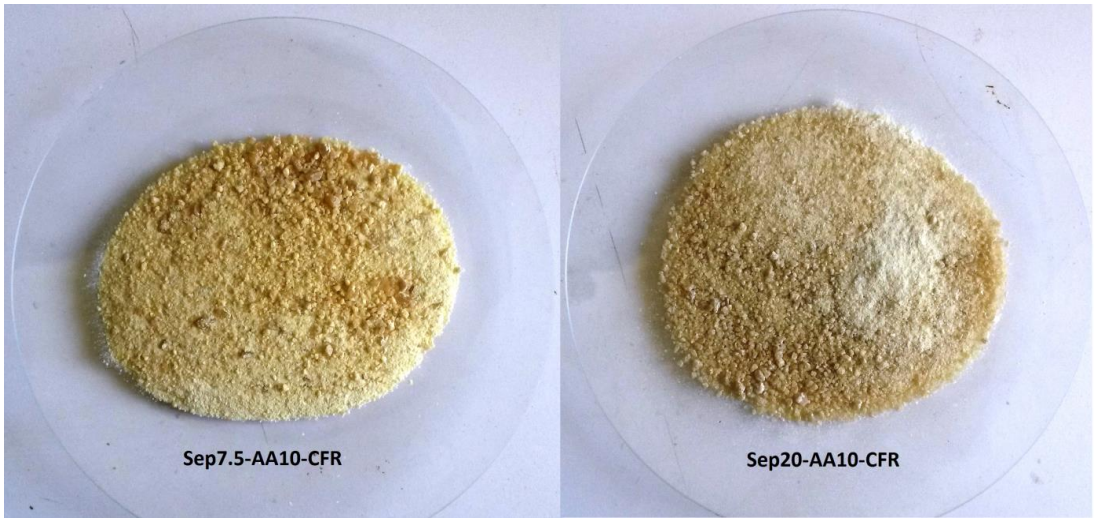


Figure 4.25 : Physical Appearance of Sep7.5-AA10-CFR and Sep20-AA10-CFR

5. CONCLUSION

In this study, fire resistance of polyurethane foam is aimed. In order to do this, clay and alendronic acid modified CFRs are synthesized. For characterization of resin and polyurethane, FT-IR, NMR, XRD, TGA and LOI are used. The chemical bonds of resins are monitored by FT-IR and NMR tests. In conclusion, it is observed that resins are synthesized successfully indicated FT-IR results. XRD showed that sepiolite modified CFRs has exfoliated structure and montmorillonite modified CFRs have intercalated structures. It is also observed that alendronic acid increased the compatibility of clay and resin, therefore alendronic acid acts as a compatibilizer when added to clay nanocomposite of CFR. Clay and phosphate addition to CFR increased the heat resistance of modified CFRs. As LOI results indicate, PU with AA10-CFR,, Sep5-CFR and PU with MM5-AA5-CFR are more resistant to fire. Especially MM5-AA5-CFR is the most effective fire retardant for PU foam.

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CURRICULUM VITAE

Name Surname: Derya Önen

Place and Date of Birth: Üsküdar-17.01.1990

E-Mail: derya.onen@hotmail.com

EDUCATION:

B.Sc.: Middle East Technical University-Chemical Engineering Graduated in 2013

PROFESSIONAL EXPERIENCE AND REWARDS:

2014-... R&D Engineer at Karbosan Zımpara Taşı Sanayi